Determining the Fate and Ecological Effects of Copper and Zinc Loading in Estuarine Environments: A Multi-Disciplinary Program CP-1156

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ACRONYMS

ASV	Anodic Stripping Voltammetry
ASV-HMDE	Anodic Stripping Voltammetry with a Hanging Mercury Drop Electrode
ASW	Artificial Seawater
BLM	Biotic Ligand Model
Chl-*a*	Chlorophyll *a*
CSC	Computer Sciences Corporation
CuCC	Copper Complexation Capacity
DOC	Dissolved Organic Carbon
DoD	Department of Defense
DPASV	Differential Pulse Anodic Stripping Voltametry
EC50	Effect concentration to 50% of the population
EN	Ethylenediamine
EPA	United States Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FY	Fiscal Year
ISE	Ion Selective Electrode
LC50	Lethal effect Concentration to 50% of the population
MESC	Marine Environmental Survey Capability
NRL	Naval Research Laboratory
pCu	Negative logarithm of the concentration of free cooper ion
pH	Negative logarithm of the concentration of hydrogen ion
RV	Research Vessel
SD-1D	One-Dimensional San Diego Bay Model
SDSUF	San Diego State University Foundation
SERDP	Strategic Environmental Research and Development Program
SIO	Scripps Institution of Oceanography
SSC SD	Space and Naval Warfare Systems Center, San Diego
TMA	Trace Metal Analyzer
TRIM-2D	Two-Dimensional Tidal Residual Intertidal Mudflat Model
TSS	Total Suspended Sediments
WER	Water Effects Ratio
WQC	Water Quality Criteria
WQS	Water Quality Standards

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This report describes the results and accomplishments of the interdisciplinary research done as part of the project "Determining the Fate and Ecological Effects of Copper and Zinc Loading in Estuarine Environments: A Multi-Disciplinary Program." This project was supported by the Strategic Environmental Research and Development Program (SERDP) under the Compliance Program, and is the project number CP-1156. The research was conducted by a team including the principal investigator, D. Bart Chadwick, and collaborators from a suite of organizations. These are: Amy Carlson, Ignacio Rivera-Duarte and Gunther Rosen from SPAWAR Systems Center San Diego (SSC-SD); Lora Kear-Padilla from Computer Sciences Corporation (CSC); Alberto Zirino from San Diego State University Foundation (SDSUF); Tom Boyd from Naval Research Laboratory (NRL); and Joris Gieskes, and Osmund Holm-Hansen from Scripps Institution of Oceanography (SIO).

The collaboration of personnel from two other projects supported by SERDP is greatly appreciated. The principal investigators and the projects are:

> Martin M. Shafer, David E. Armstrong, and Ken Ostrander, University of Wisconsin, Madison, project CP-1158, "Speciation, Sources and Bioavailability of Copper and Zinc in DoD-Impacted Harbors and Estuaries.
>
> Stephen A. Skrabal, Robert J. Kieber and William J. Cooper, University of North Carolina, Wilmington, project CP-1157, "Speciation, Fluxes, and Cycling of Dissolved Copper and Zinc in Estuaries: The roles of Sediment-Water Exchange and Photochemical Effects.'

There was a substantial number of persons that assisted with this project, and they effort is appreciated. They include Chuck Katz, Brad Davidson and Joel Guerrero from SSC-SD, Jon Groves from CSC, Peter Weber from the University of California San Diego, J. Martin Hernández-Ayón and Francisco Delgadillo from both SIO and Instituto de Investigaciones Oceanológicas, Universidad Autonoma de Baja California, Lucila Lares and Enrique Rivero from Centro de Investigación Científica y de Estudios Avanzados de Ensenada.

1 EXECUTIVE SUMMARY

Copper and zinc are two of the most ubiquitous contaminants found in many industrial and non-point source effluents that enter the marine environment. The sources of these toxic metals include discharges from facilities, ships, and small craft, as well as inputs from sediment fluxes and sediments disrupted during dredging operations and ship movements. Potential DoD sources of copper include storm waters, point sources, hull coatings, and discharges from DoD ships and facilities. Previous studies have shown that copper and zinc are highly toxic to some marine organisms. Copper and zinc discharges often exceed existing water quality criteria (WQC) or standards in the effluent and copper often exceeds WQC in the receiving systems. Compliance and clean up actions associated with copper contamination are common at DoD/Navy facilities around the country. Regulatory compliance is challenging because of the many sources, both natural and anthropogenic, and the adoption of very conservative water quality standards (WQS). Present WQC for these metals are based on concentrations of total or dissolved copper. In contrast, a large body of scientific data indicates that it is the concentration of the "free" or aqueous species (i.e., $Cu(II)_{aq}$) which correlates most closely with the toxicity of marine organisms.

This report describes results and accomplishments of the interdisciplinary research conducted in San Diego Bay from August 2000 to December 2004 by a team including personnel from SPAWAR Systems Center San Diego (SSC-SD), Computer Sciences Corporation (CSC), San Diego State University Foundation (SDSUF), Scripps Institution of Oceanography (SIO), and the Naval Research Laboratory (NRL). The goals of the research were to (1) establish the overall copper budget in the San Diego Bay for use in the development of a model that will account for the non-conservative characteristics of copper, (2) evaluate the relationship between various copper species in a prototype system, and (3) relate the observed speciation and lability to a range of biological and ecological indicators of bay health, (4) to examine the seasonal variability of the processes described in 1-3, and (5) to perform initial examinations of the distribution and lability of zinc. These goals were attained by simultaneously collecting circulation, hydrographic, water quality, copper, zinc, and biological data, at the appropriate spatial and temporal scales necessary to understand the processes controlling distributions.

In this work, a whole-basin modeling approach was developed for the prediction of the geochemical fate and ecological impact of copper on estuarine environments, mixing zones and aquatic basins. San Diego Bay was studied as a prototype system, as it provides a unique range of hydrological conditions with a relatively constant distribution of total copper concentrations, and well-defined chronic sources of copper. The bay was divided into 25 boxes or cells of about 1 km scale that match to the boxes used for the modeling effort. Also, there was a box for each Shelter Island and Commercial Basin, which are semi-enclosed marinas within the bay. Six sampling campaigns were done in order to study spatial and temporal distributions of parameters indicators of the health of the bay, as well as toxicity, complexation capacity, and physical, biological, ecological and chemical conditions. The field investigations employed a combination of real-time and laboratory analytical tools to determine the bay wide distribution of total copper and important fractions of the copper pool. These spatial distributions of copper in the bay reflect the balance of sources, flushing, and losses to the sediment. Modeling effort on these distributions allowed the development of an algorithm able to predict copper distributions and

toxicity. This algorithm can also be used to estimate the effect on copper toxicity as results of changes in the sources of copper to the bay.

Results of this work are described in detail in a series of manuscripts that were developed based on the project. These manuscripts, mentioned in the Appendix of this report, will form a significant new body of knowledge regarding the fate and effects of copper and zinc in the marine environment. A brief synopsis of the highlights of these manuscripts is provided below.

Sources of copper and zinc have been examined in detail, and previous budget estimates have been updated in accordance with the best existing data (Johnson et al., 1998; Valkirs et al., 2004; Chadwick et al., 2004). The field program for this project provided a unique and comprehensive view of water quality, with respect to copper and zinc, in relation to the hydrodynamics and residence time in the San Diego Bay over the period of approximately two years. The field effort was successful in establishing baseline water quality conditions and copper concentrations throughout the bay, and identifying locations and extent of contaminants (Blake et al., 2004; Boyd et al., 2004). As part of this effort, methodology was developed for the measurement of complexation capacity by ion selective electrode (ISE) in waters from marine harbors (Rivera-Duarte and Zirino, 2004). This developed methodology was complemented with differential pulse anodic stripping voltammetry (DPASV) to measure the spatial and temporal variation of copper complexation capacity in the bay, which were examined in relation to other characteristics of the bay and toxicity (Rivera-Duarte et al., 2005). This analysis corroborated the use of the free ion model (FIM), as the concentration of the free ion ($Cu(II)_{aq}$) is the parameter most indicative of toxic conditions in San Diego Bay (Rivera-Duarte et al., 2005). Spatial and temporal variations of copper and zinc-spiked bay water toxicity to larvae of *Mytilus galloprovincialis*, *Dendraster excentricus* and *Strongylocentrotus purpuratu* were characterized, and the results were cast in terms of the United States Environmental Protection Agency (EPA) water effects ratio (WER, Rosen et al., 2005).

Two generalized models were developed to serve as predictive tools for the fate and effects of copper. The one-dimensional, steady-state box model SD-1D provided an initial assessment the copper balance in San Diego Bay, and estimates of partitioning coefficients and of copper loss rates to the sediment. This model gives a one-dimensional, steady-state solution to the balance of conservative and non-conservative constituents. It has the advantage of rapid formulation and run-times, but lacks the ability to simulate time-varying concentrations, and has relatively coarse spatial resolution (Chadwick et al., 2004). The second numerical hydrodynamic model implemented for San Diego Bay is a depth-averaged tidal and residual circulation model known as TRIM-2D (Cheng et al., 1993). The model, predicting water surface elevations and currents produced by astronomical tides, wind, and freshwater inflows, has been calibrated using measured data from 1995-2002 (Wang, et al., 1998). TRIM-2D has the advantages of providing high spatial resolution and accounting for time-varying flows and concentrations. TRIM-2D was modified to simulate contaminant fate and transport by adding the transport equation and associated kinetic subroutines (Wang et al., in prep).

The parameters assessed with SD-1D were used in TRIM-2D for the prediction of toxicity conditions in San Diego Bay. Data from the first four surveys was used for the assessment of partitioning coefficients and rate loss to the sediments with SD-1D. These coefficients were used in TRIM-2D for the replication of the distributions of total, dissolved and particulate copper in the bay for the first four surveys. They were also used in conjunction with data for total suspended solids (TSS) and dissolved organic carbon (DOC) for the replication of the

distributions of $Cu(II)_{aq}$ in the bay for those surveys. TRIM-2D was validated by predicting the distributions of the different species of copper that were measured in the final two surveys, using the parameters developed for the first four surveys. This validation shows the capability of the model for these predictions, as the range values predicted includes those measured.

The use of TRIM-2D as a management tool for sources of copper was also proved. The model was used for the prediction of copper distributions in the case of theoretical changes in the sources of copper to the bay. While these theoretical changes are radical in nature, and practically impossible to reach, the results are plausible in nature, and indicate the most probable changes expected from these changes.

This effort is now being transitioned for the development of an integrated model that can be used by the regulatory community. There is a current effort at EPA on the development of the Biotic Ligand Model (BLM) for seawater. The BLM is already proposed for freshwater (EPA, 2003) as an alternative for the water effects ratio (WER) approach; however, this BLM needs further development for its use in seawater. The advantage of BLM over WER is economical, as it requires a substantially lower economic effort in order to produce WQS specific for each body of receiving waters. A project is being supported by the Environmental Security Technology Certification Program (ESTCP) for the development and demonstration of an integrated model for the fate and transport of toxicity by copper in Department of Defense (DoD) harbors. This project is the transitional result of the effort done under SERDP project CP-1156.

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2 OBJECTIVE

This is the final report for the effort under project CP 1156 on "Determining the Fate and Ecological Effects of Copper and Zinc Loading in Estuarine Environments: A Multi-Disciplinary Program," which is supported by SERDP. The project is a holistic, interdisciplinary and dynamic approach with a main objective of developing the methodology for predicting the geochemical fate and ecological effects of copper and zinc in coastal embayments. The objective of the work described in this report is to conduct "research that will provide the Services a means to identify harbor and estuarine areas that are at the greatest risk from copper or zinc discharges and sediment disturbances" (SERDP, 2000). While there have been a number of laboratory and localized field studies to evaluate the speciation and effects of these heavy metals on marine organisms, there are few studies that evaluate the fate of their releases on an entire coastal embayment. In addition, there are few studies that have explored the relative importance of the physical transport and chemical transformation time scales that regulate the fate and effects of copper and zinc. San Diego Bay is being studied as prototype embayment, as it provides a unique range of hydrological conditions with a relatively constant distribution of total copper concentrations; however, the resulting model should be applicable to other estuarine environments impacted by DoD activities.

This report describes results and accomplishments of the interdisciplinary research conducted in San Diego Bay from August 2000 to December 2004 by a team including personnel from SPAWAR Systems Center San Diego (SSC-SD), Scripps Institution of Oceanography (SIO), and the Naval Research Laboratory (NRL). The goals of the research were to (1) establish the overall copper budget in the San Diego Bay for use in the development of a model that will account for the non-conservative characteristics of copper, (2) evaluate the relationship between various copper species in a prototype system, and (3) relate the observed speciation and lability to a range of biological and ecological indicators of bay health, (4) to examine the seasonal variability of the processes described in 1-3, and (5) to perform initial examinations of the distribution and lability of zinc. These goals were attained by simultaneously collecting circulation, hydrographic, water quality, copper, zinc, and biological data, at the appropriate spatial and temporal scales necessary to understand the processes controlling their distributions.

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3 BACKGROUND

Copper and zinc are ubiquitous contaminants in heavily used coastal embayments. Sources of copper and zinc include leaching from antifouling paints, industrial and municipal discharges, ship discharges, atmospheric fallout, storm water, and fluxes from benthic sediments. The combination of continuous inputs and low flushing renders these coastal embayments as places with high loading of copper and zinc that can exceed the WQC assigned for these bodies of water. Improved understanding of the processes that control the mass balance, fate and effects of copper and zinc in these environments is important to the development and implementation of coastal management and pollution control strategies. While there have been a number of laboratory and localized field studies to evaluate the speciation and effects of copper and zinc on marine organisms, there are few studies that evaluate the fate of copper and zinc releases on an entire coastal embayment. In addition, there are few studies that have explored the relative importance of the physical transport and chemical transformation time scales that regulate the fate and effects of copper and zinc.

Here we present the results and accomplishments of a study to measure, describe, model and predict the potential toxic effects of copper and zinc discharges to San Diego Bay from a whole-basin perspective. Detailed components of this effort are presented in a series of separate publications, and the reader is directed to them for in-depth descriptions of methodology, measurements, discussions and predictions. These manuscripts, which are either published, or in press, include: Blake et al. (2004), Chadwick et al. (2004), Rivera-Duarte and Zirino (2004), Boyd et al. (2005), Rivera-Duarte et al. (2005), and Rosen et al. (2005). The purpose of this report is to provide an overall view of this work, an evaluation of the predictive capacity of the algorithm developed by this effort, as well as a description of the work to be developed as transition of this project.

In this work, whole-basin modeling approach was developed for the prediction of the geochemical fate and ecological impact of copper and zinc on estuarine environments, mixing zones and aquatic basins. San Diego Bay was studied as a prototype system, as it provides a unique range of hydrological conditions with a relatively constant distribution of total copper concentrations, and well-defined chronic sources of copper. The bay was divided into 25 boxes or cells of about 1 km scale that match to the boxes used for the modeling effort. Also, there is a box for each Shelter Island and Commercial Basin, which are semi-enclosed marinas within the bay (Figure 1). Six sampling campaigns were done in order to study spatial and temporal distributions of parameters indicators of the health of the bay, as well as toxicity, complexation capacity, and physical, biological, ecological and chemical conditions (Figure 2). The field investigations employed a combination of real-time and laboratory analytical tools to determine the bay wide distribution of total copper and important fractions of the copper pool. These spatial distributions of copper in the bay reflect the balance of sources, flushing, and losses to the sediment. Modeling effort on these distributions allowed the development of an algorithm able to predict copper distributions and toxicity. This algorithm could also be used to estimate the effect on copper toxicity as results of changes in the sources of copper to the bay.

The effort for the study of copper toxic effects in San Diego Bay is based on the assumption that the free aqueous copper ion ($Cu(II)_{aq}$) better represents the bioavailable fraction of copper to organisms, than either the total or dissolved copper concentrations. This is predicted by the Free

Ion Model of Buffle et al (1990; Figure 3), and has been confirmed by experimental evidence (Sunda and Guillard, 1976; Sunda and Ferguson, 1983; Campbell, 1995; Moffet and Brand, 1996; Ericksen et al, 2001; Rivera-Duarte et al, 2005). The model suggests that the chemical partitioning among the different copper chemical species, including the concentration of $Cu(II)_{aq}$, are regulated by both the total copper concentration (Cu_t) and the natural buffer capacity (i.e., the amount of ligands, L, available to bind copper, or the copper complexation capacity, Cu-CC) of the system. The model also suggests that $Cu(II)_{aq}$ is the only chemical species available to the organisms, and it represents the toxic fraction of the copper in seawater. Therefore the bioavailability and toxicity of copper in marine environments depend on both the total copper concentration and the complexation capacity.

The prediction of the concentration of $Cu(II)_{aq}$ is the base for the management of the sources of copper in the bay. As the toxicity of copper is better related to $Cu(II)_{aq}$ than to either the total or dissolved copper, the modeling and prediction of copper toxicity could be used to predict the effect of modifications to the sources of copper to the bay. This may be relatively easier in San Diego Bay as the concentration distributions of both total and dissolved copper are at steady state.

4 TECHNICAL APPROACH

Water distributions in San Diego Bay were examined using the SSC-SD Marine Environmental Survey Capability (MESC), a real-time environmental data mapping system. A series of six surveys were completed over two annual cycles including summer, winter and spring conditions (30 August 2000, 30 January 2001, 11 May 2001, 19 September 2001, 27 February 2002, 14 May 2002). The surveys covered the entire bay (Figure 1). Circulation and hydrographic measurements included current velocity, salinity, temperature, density, and sample depth. Conventional water quality parameters included light transmission, dissolved oxygen, pH, fluorescence, chlorophyll *a* (Chl-*a*), and nutrients. Measurements of copper included the total copper, the dissolved fraction, the pH 2 and pH 8 extractable fractions, and the ionic fraction. Measurements of zinc included the total zinc, dissolved fraction, and pH 5 extractable fraction. Metal speciation measurements were supported by evaluation of copper and zinc binding ligands using ISE and DPASV titration techniques, as well as measures of other potential binding substrates including DOC, TSS, and suspended particle size distribution. Biological assessment was carried out from two primary perspectives including traditional laboratory toxicity bioassays, and also via characterization of bacterial and phytoplankton communities within the bay.

Results were integrated into two complementary modeling systems and are being used to assess the mass balance, fate and toxicity of copper in San Diego Bay (Figure 4). Using the information from the initial four surveys, the one-dimensional, steady-state box model SD-1D provided an initial assessment of the copper balance in San Diego Bay, provided estimates of the partitioning coefficients and estimates of copper loss rates to the sediment. This model gives a one-dimensional, steady-state solution to the balance of conservative and non-conservative constituents. It has the advantage of rapid formulation and run-times, but lacks the ability to simulate time-varying concentrations, and has relatively coarse spatial resolution (Chadwick et al., 2004). For this application, the model was segmented into a series of 25 boxes along the axis of the bay, resulting in a spatial resolution of about 1 km. Two side basin boxes (Shelter Island (6) and Commercial Basin (9)) were also designated for sampling purposes, but were not evaluated in the model. These boxes corresponded with the sampling grid for the field sampling program (Figure 1).

The second numerical hydrodynamic model implemented for San Diego Bay is a depth-averaged tidal and residual circulation model known as TRIM-2D (Cheng et al., 1993). The model, predicting water surface elevations and currents produced by astronomical tides, wind, and freshwater inflows, has been calibrated using measured data from 1995-2002 (Wang, et al., 1998). TRIM-2D has the advantages of providing high spatial resolution and accounting for time-varying flows and concentrations. TRIM-2D was modified to simulate contaminant fate and transport by adding the transport equation and associated kinetic subroutines. Specifically, TRIM-2D has been used to simulate fate and transport of various contaminants in San Diego Bay, including copper effluent discharge off the Convention Center (Wang and Chadwick, 1998), copper and biocide dispersion simulation for anti-fouling ship hull paint (Wang et al., 2002), and dispersion of sewage spills in the Bay. The model was validated by predicting the distributions of the suite of copper species for the last two surveys, using the actual TSS and DOC data for those surveys, and the suite of partitioning and loss parameters developed for the

first four surveys. These studies show that the model is accurate and stable for fate and transport of both conservative and non-conservative contaminants in San Diego Bay (Wang et al., in prep).

5 RESULTS AND ACCOMPLISHMENTS

The objectives of the project for the development of a model able to predict toxicity in San Diego Bay were met. As mentioned above, the objectives were to (1) establish the overall copper budget in San Diego Bay, (2) evaluate the relationship between various copper species, (3) relate the observed speciation and lability to a range of biological and ecological indicators of bay health, (4) to examine the seasonal variability of the processes described in 1-3, and (5) to perform initial examinations of the distribution and lability of zinc. The results for these objectives are explained in the following sections. However, as this research resulted in a series of publications, the reader is directed to these for an in-deep description and analysis. These publications are: Blake et al. (2004), Chadwick et al. (2004), Rivera-Duarte and Zirino (2004), Boyd et al. (2005), Rivera-Duarte et al. (2005), and Rosen et al. (2005).

Sources of Copper

The main source of copper to the bay is leaching from antifouling paint. Copper inputs to San Diego Bay are clearly identified and evaluated to a good degree of certainty. The estimates presented here were based on compilations on copper releases from civilian and Navy hull coating leachates, civilian and Navy hull cleaning, other ship discharges (e.g. cooling water), point-source discharges, stormwater runoff, and atmospheric deposition (Johnson et al., 1998; PRC, 1997). These estimates were updated to account for recent improvements in estimates for various input rates and to incorporate estimates for particulate copper (Figure 4).

In response to the compilation of measurements from Seligman et al. (2001), and Valkirs et al (2003), the estimates for Navy hull coating leachate were updated to 3.8 $\mu g\ cm^{-2}\ d^{-1}$, and civilian and commercial hull leachate was updated to 8.2 $\mu g\ cm^{-2}\ d^{-1}$, instead of 17 $\mu g\ cm^{-2}\ d^{-1}$ previously used for both of these releases (Johnson et al., 1998). The input of dissolved copper from civilian hull cleaning was updated based on a new discharge rate of 6 $\mu g\ cm^{-2}\ cleaning^{-1}$ reported by Schiff and Diehl (2002). Navy and civilian hull cleaning inputs for particulate copper were calculated from the dissolved estimates by applying the particulate:dissolved ratio reported in EPA (1998). Atmospheric and direct rainfall inputs were calculated following PRC (1997), but were apportioned to each box based on surface area. Stormwater inputs of dissolved copper were updated to use measured event mean concentrations for all available watersheds with the remaining areas calculated following the simple model method described by Johnson et al. (1998). Particulate copper loading from base flow and stormwater were calculated using the particulate: dissolved ratio for event mean concentrations reported by Woodward-Clyde (1996). The results of this analysis indicate total copper loadings of about 20,400 kg y^{-1} and 22,000 kg y^{-1} for dry weather and wet weather conditions respectively, and that releases from antifouling paint are the main source of copper, up to 65%, within the bay (Chadwick et al., 2004; Figure 5).

The distribution of copper sources in the bay is localized. The distribution of vessels seems to be the main factor affecting the distribution of copper sources in the bay (Figure 5). While the outer part of the bay (boxes 1 to 17) is dominated by pleasure boat sources, the inner part (boxes 18 to 27) is dominated by ship (i.e., commercial and military) sources.

Spatial and Temporal Variations Copper Distribution

Overall, the results of this study of copper in San Diego Bay indicate that for most of the bay during most of the year copper exposure is regulated to levels below toxic thresholds by a combination of factors including natural complexation, partitioning and settling. Exceptions to this occur in certain areas of the bay, such as yacht harbors where there is a combination of strong sources and poor flushing. Also during conditions of low concentration of complexing materials, such as suspended matter, larger areas of the bay may experience free copper levels that approach toxic thresholds.

Results from these campaigns show that hypersaline steady state conditions are predominant in San Diego Bay from summer to fall (Blake et al, 2004; Chadwick et al., 2004). These hypersaline conditions are generally associated with healthier conditions of lower free copper ion concentrations and large values of EC50 than the observed copper concentrations (Rivera-Duarte et al, 2005; Rosen et al., 2005). In contrast, closer-to-toxic conditions where observed in the bay two weeks after a rain event in winter (January 2001). The input of freshwater developed weak estuarine conditions, with low chlorophyll and total suspended solids, higher concentrations of free copper ion, and values of EC50 very close to those of copper concentrations.

Measured concentrations of dissolved copper indicate a near steady-state balance in San Diego Bay. This is indicated by measurements done through the last couple of decades by different researchers (Zirino et al., 1978; Flegal and Sañudo-Wilhelmy, 1993, Esser and Volpe, 2002) and by our effort. These measurements are presented in Figure 6, which shows box and whiskers plots of these data. In each plot the box indicates the median and the 25th and 75th percentiles, and the whiskers indicate the 10th and 90th percentiles of the data, outlying data is also shown. Most of the data is from filtered ($\leq$0.45 µm) samples, but that from Zirino et al. (1978), which was measured from unfiltered samples by DPASV; however, as is our experience that these measurements represent those of the dissolved copper, then these were used in the comparison. In general, the median concentration of dissolved copper in the northern region of the bay has remained constant at about 2 $\mu g\ L^{-1}$.

There is a continuous increase in total and dissolved copper concentrations from the mouth to the back of the bay. Concentrations at the mouth are representative of the influence of the adjacent coastal waters, with concentrations in the range of 0.1 to 0.4 $\mu g\ L^{-1}$ (Zirino et al., 1978; Flegal and Sañudo-Wilhelmy, 1993, Esser and Volpe, 2002; Blake et al., 2004; Rivera-Duarte et al, 2005). These concentrations increase to the back of the bay, reaching dissolved copper concentrations above the saltwater WQC for the protection of aquatic life of 3.1 $\mu g\ L^{-1}$ (EPA, 1996) in the middle of south bay, and decreasing to the very back of the bay (Blake et al., 2004; Rivera-Duarte et al, 2005). Total copper shows similar spatial distributions to those of dissolved copper. The increase in copper concentration is linked to the similar increase in hydraulic residence time into the back of the bay (Chadwick et al., 2004).

In contrast to the distributions of total and dissolved copper, free copper ion ($Cu(II)_{aq}$) decreases in concentration to the back of the bay. The evidence indicates this is a result of the increase in binding materials to the back of the bay, and while $Cu(II)_{aq}$ represents only a very small fraction of the total copper concentration, this fraction is critical as it better represents the amount of copper available to organisms (Rivera-Duarte et al., 2005).

Distribution of Copper Complexation Capacity

The natural buffering capacity to attenuate the bioavailability of copper, or copper complexation capacity (Cu-CC), had values similar to those reported for other coastal environments. While Cu-CC was measured with an ISE, in contrast to the commonly used voltammetric techniques, the range in concentration measured is consistent with that measured for other coastal bodies of water (Figure 7).

Spatial distributions of Cu-CC indicate an increase in concentration of ligands going into the bay. This distribution is similar to that of total copper, and results in a decrease in $Cu(II)_{aq}$ (i.e., less copper bioavailable) into the bay (Rivera-Duarte et al., 2005). The effect of Cu-CC on the bioavailability of copper is also confirmed by the distribution of EC50 (i.e., the amount of copper needed to affect the development of 50% of the larval population), which also increases into the bay (Rosen et al., 2005).

Natural buffer capacity keeps the concentration of $Cu(II)_{aq}$ below a toxic threshold level. Calculation of the concentration of $Cu(II)_{aq}$ at the EC50 level indicate that about 1×10^{-11} M $Cu(II)_{aq}$ (pCu ≥ 11) are needed to have this deleterious effect (Rivera-Duarte et al., 2005). In contrast, concentrations of $Cu(II)_{aq}$ measured in the bay systematically stay below this level (Figure 8), but in a single sample event done two weeks after a strong rainfall event (January 2001). These results indicate that natural copper complexation capacity keeps the bioavailable fraction of copper below toxic levels.

Distribution of Toxicity

General ambient conditions in the bay are not toxic (Rosen et al., 2005). This is evidenced by embryo-larval development toxicity tests with bivalve (*Mytilus galloprovincialis*) and/or echinoderms (*Strongylocentrotus purpuratus* or *Dendraster excentricus*), which are the organisms more sensitive to copper. The results for these larval-development tests in waters of the bay with no extra copper added, representing the present state of the bay, show that in average 93 ± 5% of the larvae reached normal development in 48 to 72 hours over the course of the study. Therefore, even though some of these samples exceeded the WQC, conditions in waters of the bay are consider non-toxic for these larvae.

The concentration of copper needed to reach a specific toxicity end-point (i.e. EC50) increases from the mouth to the head of the bay. Mean EC50 by the head of the bay averaged 1.65 ± 0.33 times higher than those from the mouth. This distribution presented some temporal variation, with a smallest difference in May 2002 by a factor of 1.36, and the largest difference in August 2000 by a factor of 2.18. The increase in EC50 into the bay indicates a similar gradient in complexation capacity, which is consistent with the trends in DOC and TSS.

There is a trend at EPA to recognize the need for regulation based on the bioavailable fraction of metal (EPA, 2003). This is done following either a theoretical or a practical approach. The theoretical approach is used only in freshwaters, and is based on the BLM, which estimates the critical (i.e., toxic) concentration of copper by considering the concentrations and binding strength of cations that compete with free metal ion at the biotic ligand (e.g. fish gill; DiToro et al., 2001). This toxic fraction of copper is also related to the concentrations in the water of total dissolved copper and complexing ligands, as the biotic ligand competes for copper with complexing ligands, other metals and other cations in the water. The use of the BLM improves

on the characterization of the toxic effects of copper, as it incorporates environmental conditions that are more representative of each specific body of freshwater. Therefore, by measuring a fairly low number of environmental parameters (i.e., hardness, alkalinity, dissolved organic carbon (DOC), total dissolved metal concentration, major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and major anions (SO_4^{2-}, Cl^{-})) in the freshwater it is possible to estimate the specific critical concentration that will be toxic to the organism.

The currently accepted practical regulatory approach for seawaters is the WER (EPA, 1994). This method addresses the differences in natural buffering capacities by comparing toxicity of metal added to effluents or receiving waters with identical exposures in laboratory water similar to that used for the development of the WQC. The ratio of the toxic levels (e.g., EC50 or lethal effect concentration to 50% of the population, LC50) between the exposures is then used as multiplier of the national WQC criterion to derive a site-specific criterion. This criterion now includes the differences in natural buffering capacities of both waters. A positive WER indicates that the national WQC is overprotective to the specific body of water, and a negative WER indicates under protection. For San Diego Bay as a whole, estimates for total recoverable and dissolved WERs ranged from 2.07 to 2.27 and 1.63 to 1.80, respectively, suggesting that national WQC for copper are overly conservative in this bay, and that a site-specific copper standard would be more representative of conditions in this receiving system (Rosen et al., 2005).

Copper Fate and Transport Modeling

Two complementary modeling systems were used to assess the mass balance and fate of copper in San Diego Bay (Figure 4). The one-dimensional, steady-state box model SD-1D provided an initial assessment of the copper balance in San Diego Bay, and estimates of copper partitioning coefficients and loss rates to the sediment. This model gives a one-dimensional, steady-state solution to the balance of conservative and non-conservative constituents. It has the advantage of rapid formulation and run-times, but lacks the ability to simulate time-varying concentrations, and has relatively coarse spatial resolution (Chadwick et al., 2004). For this application, the model was segmented into a series of 25 boxes along the axis of the bay (Figure 1), resulting in a spatial resolution of about 1 km. Two side basin boxes (Shelter Island (6) and Commercial Basin (9)) were also designated for sampling purposes, but were not evaluated in the model. These boxes corresponded with the sampling grid for the field sampling program.

The second numerical hydrodynamic model implemented for San Diego Bay is a depth-averaged tidal and residual circulation model known as TRIM-2D (Cheng et al., 1993). The model, predicting water surface elevations and currents produced by astronomical tides, wind, and freshwater inflows, has been calibrated using measured data from 1995-2002 (Wang, et al., 1998). TRIM-2D has the advantages of providing high spatial resolution and accounting for time-varying flows and concentrations. TRIM-2D was modified to simulate contaminant fate and transport by adding the transport equation and associated kinetic subroutines. Specifically, TRIM-2D has been used to simulate fate and transport of various contaminants in San Diego Bay, including copper effluent discharge off the Convention Center (Wang and Chadwick, 1998), copper and biocide dispersion simulation for anti-fouling ship hull paint (Wang et al., 2002), and dispersion of sewage spills in the bay. These studies show that the model is accurate and stable for fate and transport of both conservative and non-conservative contaminants in San Diego Bay.

For both models, copper loadings were determined based on the estimates of Johnson et al. (1998) that were updated to account for recent improvements in estimates for various input rates, and to incorporate estimates for particulate copper (see Section on Sources of Copper). The results of this analysis indicate total copper loadings of about 20,400 kg yr^{-1} and 22,000 kg yr^{-1} for dry weather and wet weather conditions respectively. Spatially these sources are fairly evenly distributed throughout the bay (Figure 6), and are dominated by releases associated with antifouling coatings (Figure 5). With the transport and mixing characteristics determined by the calibrated models, and the loadings and ocean boundary conditions defined, the total copper balance depends only upon the loss rate of copper from the water column to the sediment. The SD-1D model was used to evaluate three possible loss scenarios including: (1) zero loss; (2) a uniform, first-order loss rate; and (3) a simple particle-settling model. The particle-settling model was shown to provide the best performance. Coefficients for the loss rate were developed by best fit to the field data using the SD-1D model, which were then applied to TRIM-2D.

Model results were compared with field data and it was demonstrated that, in general, model results resemble measurements for all the copper species, including particulate, dissolved, free copper and total copper. Predicted (and measured) total copper concentrations increase from the mouth with a total copper concentration of ~ 0.3 μg L^{-1} toward the southern portion of the Bay (Figure 10 thru Figure 13). Concentrations of total copper reach maximum (about 2.8-3.3 μg L^{-1}) in the mid south bay, and then drop slightly to ~ 1.5-2.5 μg L^{-1} going further south. Such general trends seem to persist for all the periods, a phenomenon exhibited by both measured data and model results.

The TRIM-2D model resolves a number of "hot spots" in the marinas, including Shelter Island, West Harbor Island, Glorietta Bay, and Coronado Cays, where total copper concentrations reaching up to 4-8 μg L^{-1}, exceeding the 3.1 μg L^{-1} criteria (Figure 10 thru Figure 13). High concentrations in these marinas result primarily from the poor flushing due to the confined configuration of these water bodies, in combination with the high concentration of sources in these areas. For the same reason, hydrodynamic conditions in these water bodies are much less energetic than those in the open bay water. Therefore, settling of particulate matters, including copper, are more statistically likely (easier) inside the marina than the open bay water. For this study, we did not link settling velocity to hydrodynamic conditions, which requires further study to better describe the settling process in estuaries, which is controlled by hydrodynamics.

The model results indicate that the overall fate of copper in the bay is balanced between exchange with the ocean and loss to the sediment (Chadwick et al., 2004). Integration of the sediment load throughout the bay indicates a total loss of about 9,700 kg yr^{-1} to the sediments. Of the 9,700 kg yr^{-1} that enters the sediment, 83% is to the inner bay, while only 17% is to the outer bay. In contrast, only 57% of the loading is to the inner bay, while 43% is to the outer bay. Given the total annual loading of copper to the bay of about 20,400 kg yr^{-1}, this balance suggests that about 48% of the input is transported to the sediment, while the remaining 52% is flushed to the ocean.

Following the verification process summarized above, the TRIM-2D model was used to examine two hypothetical source reduction scenarios for the Bay. In the first scenario, all sources related to antifouling releases from Navy vessels were removed. This scenario represents the potential outcome of the implementation of alternative coatings on Navy vessels. The results show that total copper concentrations in the mid to south bay would be substantially reduced; however, no significant reduction would occur in the marina side-basin areas (Figure 14). In the second

scenario, all antifouling sources were removed (Navy and pleasure boats), representing the case of bay-wide implementation of alternative coatings. In this case, concentrations throughout the bay are predicted to be substantially lower than current levels (Figure 14). Thus, the algorithm developed in this effort could be used as a tool for the management of sources to San Diego Bay as a whole.

Distribution and Lability of Zinc

As indicated by Shaffer et al. (2004), in San Diego Bay the concentrations and speciation of zinc contrasts with those for copper. While both elements present similar distributions, copper concentrations could reach toxic effects, while those of zinc are as far as one order of magnitude below those levels. And, while the fraction of $Cu(II)_{aq}$ is very minimal (<0.01%), that for the free zinc ion seems to dominate in the bay.

Concentrations of zinc in San Diego Bay are among the largest measured in coastal embayments (Figure 15). Dissolved zinc concentrations measured in our effort are in the range from 0.10 to 13 $\mu g\ L^{-1}$, which agree with those reported for San Diego Bay by other researchers (0.26 to 11 $\mu g\ L^{-1}$; Esser and Volpe, 2002; Shaffer et al., 2004), and are one to two orders of magnitude larger than zinc concentrations in neighbor coastal waters (0.01 to 0.07 $\mu g\ L^{-1}$; Sañudo-Wilhelmy and Flegal, 1991). Zinc concentrations in San Diego Bay are also up to an order of magnitude larger that those reported for San Francisco Bay (0.24 to1.8 $\mu g\ L^{-1}$; Flegal et al., 1991) and Galveston Bay (0.3 to 4.5 $\mu g\ L^{-1}$; Morse et al., 1993), which should be considered very similar with respect to anthropogenic inputs to San Diego Bay. Only the zinc concentrations measured in the Elizabeth River Estuary (0.32 to 11 $\mu g\ L^{-1}$; Wei et al., 2003) are comparable to those in San Diego Bay.

Spatial distributions of zinc in the bay follow the general increase into the back of the bay pattern observed for copper (Figure 16). Concentrations of total and dissolved zinc increase into the back of the bay, with the lowest values in the area by the mouth of the bay influenced by neighbor coastal waters. Zinc concentrations increase further close to the mouth of the bay than those for copper, and also have a steeper decrease to the back of the bay than copper concentrations (Figure 16). Another different characteristic in comparison to copper distributions is the seasonal change in concentrations. While copper distributions are at steady-state (Blake et al., 2004; Rivera-Duarte et al., 2005), zinc distributions have larger concentration values in the winter than the rest of the year (Figure 16).

Waters in San Diego Bay are not toxic with respect to zinc concentrations. In spite of the extremely high zinc concentrations in the bay, toxicity tests and the WQC indicate that these concentrations are one order of magnitude lower than those harmful to aquatic organisms. Toxicity tests with larvae of *Strongylocentrotus purpuratus* and *Mytilus galloprovincialis* with waters of San Diego Bay indicate that about 100 or 250 $\mu g\ L^{-1}$ of zinc are needed to reach a larval-development EC50, respectively. Also, the largest zinc concentrations measured in San Diego Bay are five-fold lower than EPA chronic WQC (81 $\mu g\ L^{-1}$; EPA 2002). These results indicate that waters in San Diego Bay are at a healthy level with respect to zinc concentrations.

In comparison with copper, most of the zinc is present as free ion in San Diego Bay. While a minimal (<0.01%) of the copper is present as free ion, most of the zinc is free ion, as indicated by attempts to measure the zinc complexation capacity. This was done by anodic stripping voltammetry with a hanging mercury electrode (ASV-HMDE) and titrations with zinc, which

indicate an increase in free zinc ion correspondent to the additions, in contrast to the expected result when natural ligands are able to keep the concentration of free zinc ion constant (Figure 17). In principle this result could imply that zinc does not follows the free ion model; however, this result could also imply that the toxic concentration of free zinc ion is at least five fold higher than the maximum dissolved zinc concentration observed in the bay.

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6 SUMMARY

Detailed descriptions of the overall sampling design and technical approach for the project have been provided in previous annual reports. Below we provide a brief summary of recent accomplishments based on a set of developing or submitted manuscripts. These manuscripts are provided in the Appendix to document the bulk of the work performed in this project.

Section 5.1 describes efforts to refine the loading estimates of copper to San Diego Bay. Building from the previous work of Johnson et al. (1998) we have refined the copper budget for all important components. Copper inputs to San Diego Bay are clearly identified and evaluated to a good degree of certainty. The estimates presented here were based on compilations on copper releases from civilian and Navy hull coating leachates, civilian and Navy hull cleaning, other ship discharges (e.g. cooling water), point-source discharges, stormwater runoff, and atmospheric. These estimates were updated to account for recent improvements in estimates for various input rates, and to incorporate estimates for particulate copper. The results of this analysis indicate total copper loadings of about 20,400 kg y^{-1} and 22, 000 kg y^{-1} for dry weather and wet weather conditions respectively, and that releases from antifouling paint are the main source of copper, up to 65%, within the bay (Chadwick et al., 2004).

Section 5.2 presents the completed effort to characterize the spatial and temporal variations in the distribution of copper in San Diego Bay. Overall, the results of this study of copper in San Diego Bay indicate that for most of the bay during most of the year copper exposure is regulated to levels below toxic thresholds by a combination of factors including natural complexation, partitioning, flushing and settling. Exceptions to this occur in certain areas of the bay, such as yacht harbors where there is a combination of strong sources and poor flushing. Also during conditions of low concentration of complexing materials, such as suspended matter, larger areas of the bay may experience free copper levels that approach toxic thresholds (Blake et al, 2004; Chadwick et al., 2004).

Section 5.3 examines the distribution of copper complexation capacity in San Diego Bay. The natural buffering capacity to attenuate the availability of copper, or copper complexation capacity (Cu-CC), had values similar to those reported for other coastal environments. While Cu-CC was measured with an ion selective electrode (ISE), in contrast to the commonly used voltammetric techniques (i.e., DPASV), the range in concentration measured is consistent with that measured for other coastal bodies of water. Spatial distributions of Cu-CC indicate an increase in concentration of ligands going into the bay. This distribution is similar to that of total copper, and results in a decrease in $Cu(II)_{aq}$ (i.e., less copper bioavailable) into the bay. The effect of Cu-CC is also confirmed by the distribution of EC50 (i.e., the amount of copper needed to affect the development of 50% of the larval population), which also increases into the bay. Natural buffer capacity keeps the concentration of $Cu(II)_{aq}$ below a toxic threshold level, and our results indicate that a $Cu(II)_{aq}$ concentration of 1×10^{-11} M (i.e., pCu $\geq$ 11) or higher is needed in order to achieve the toxic level used in regulatory purposes (Rivera et al., 2005).

Section 5.4 describes the distribution of toxicity in San Diego Bay waters. General ambient conditions in the bay are not toxic (Rosen et al., 2004). This is evidenced by embryo-larval development toxicity tests with bivalve (*Mytilus galloprovincialis*) and/or echinoderms (*Strongylocentrotus purpuratus* or *Dendraster excentricus*), which are the organisms more sensitive to copper. Even though some of these samples exceeded the WQC, conditions in water

of the bay are consider non-toxic for these larvae. The concentration of copper needed to reach a specific toxicity end-point (i.e. EC50) increases from the mouth to the head of the bay. The increase in EC50 into the bay indicates a similar gradient in complexation capacity, which is consistent with the trends in dissolved organic carbon and total suspended solids. These variations were also examined under the currently accepted practical regulatory approach for seawaters, the water-effect-ratio (WER; EPA, 1994). This method addresses the differences in natural buffering capacities by comparing toxicity of metal added to effluents or receiving waters with identical exposures in laboratory water similar to that used for the development of the WQC. For San Diego Bay as a whole, estimates for total recoverable and dissolved WERs indicate that the national WQC for copper are overly conservative in this bay, and that a site-specific copper standard would be more representative of conditions in this receiving system.

Section 5.5 describes the effort in copper fate and transport modeling. Two complementary modeling systems were used to assess the mass balance and fate of copper in San Diego Bay. The one-dimensional, steady-state box model SD-1D provided an initial assessment of the copper balance in San Diego Bay, and estimates of copper loss rates to the sediment. The second numerical hydrodynamic model implemented for San Diego Bay is a depth-averaged tidal and residual circulation model known as TRIM-2D (Cheng et al., 1993). The model, predicting water surface elevations and currents produced by astronomical tides, wind, and freshwater inflows, has been calibrated using measured data from 1995-2002 (Wang, et al., 1998). TRIM-2D has the advantages of providing high spatial resolution and accounting for time-varying flows and concentrations. TRIM-2D was modified to simulate contaminant fate and transport by adding the transport equation and associated kinetic subroutines. Both models have now been calibrated and validated to accurately simulate transport, speciation and fate of copper in San Diego Bay (Chadwick et al., 2004; Chadwick et al., in prep; Wang et al., in prep).

7 CONCLUSIONS

This report describes progress on interdisciplinary research conducted in San Diego Bay from August 2000 to December 2004 by a team including personnel from SSC-SD, SIO, SDSUF, and NRL. The goals of the research are to (1) establish the overall copper budget in the San Diego Bay for use in the development of a model that will account for the non-conservative characteristics of copper, (2) evaluate the relationship between various copper species in a prototype system, and (3) relate the observed speciation and lability to a range of biological and ecological indicators of bay health, (4) to examine the seasonal variability of the processes described in 1-3, and (5) to perform initial examinations of the distribution and lability of zinc. These goals are being realized by simultaneously collecting circulation, hydrographic, water quality, copper, zinc, and biological data, at the appropriate spatial and temporal scales necessary to understand the processes controlling distributions. Conclusions that can be drawn based on the work to date are described in detail in the manuscripts that form the Appendix of this report. A brief synopsis of the highlights of these manuscripts is provided below.

- Significant progress has been made in refining the source budget of copper. This is a critical model input parameter, and also a critical management parameter for copper in Navy harbors. The resulting budget has been incorporated into a publication for the mass balance model (Chadwick et al., 2004).
- The field program for this project was successfully completed, and the results have been published (Blake et al., 2004). This data represents one of the most comprehensive spatial and temporal descriptions of copper and zinc and a harbor system, and will provide the basis for future assessment of new regulatory tools such as the Biotic Ligand Model.
- The distribution of copper complexation capacity in the bay has been carefully examined and described (Rivera-Duarte et al., 2005). These results indicate that natural copper complexation capacity keeps the bioavailable fraction of copper below toxic levels in ambient waters of the bay.
- The variation in copper toxicity to relevant, sensitive marine species as been successfully documented in relation to both copper concentration, copper complexation capacity and other water quality characteristics (Rosen et al., 2005). General ambient conditions in the bay are not toxic to the most sensitive marine species. WERs on the order of 1.63 to 2.27 indicate that national WQC for copper are overly conservative in this bay, and that a site-specific copper standard would be more representative of conditions in this receiving system.
- One and two-dimensional models have been implemented and validated for copper in San Diego Bay (Chadwick et al., 2004; Chadwick et al., in prep; Wang et al., in prep). The models have been used to examine the partitioning, settling, and overall mass balance of copper in the bay. The models have also been used to examine the speciation and toxicity of copper. Finally, the models have been used to examine hypothetical future loading scenarios to demonstrate their utility as management tools.

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8 TRANSITION

As thoroughly discussed and explained in the previous sections, the main accomplishment of project CP-1156 was the development and validation of a fate and transport model able to estimate the development of toxic conditions in San Diego Bay. These toxic conditions are modeled from the concentration of $Cu(II)_{aq}$ in those waters. There is a great deal of research that supports the use of $Cu(II)_{aq}$ as indicative of toxic effects in seawater (Sunda and Guillard, 1976; Sunda and Ferguson, 1983; Campbell, 1995; Moffet and Brand, 1996; Seligman and Zirino, 1998; Eriksen, et al., 2001; Zirino, and Seligman, 2002; Rivera-Duarte et al., 2005). However, at this time the regulatory effort is not based on the concentration of $Cu(II)_{aq}$, but is following two different approaches. As indicated in the section of Results and Accomplishments above, EPA is following the BLM for freshwaters and a WER approach in seawater. Both of these approaches are directed to figure out the effect of the natural conditions in the receiving body of water in comparison to the characteristics of the laboratory water used for the development of WQC. This is they are used for the development of quality criteria specific for a receiving body of water. The main difference between these approaches is that WER requires a significant use of economic resources for its development, while the BLM is a modeling effort that requires substantially less economic resources to reach a similar result. There is also a substantial interest at EPA on the development of a BLM for seawater.

There is a great deal of similitude between the free ion model and the BLM. As indicated above, the use of $Cu(II)_{aq}$ as indicator of toxicity has been substantiated by several researchers. And, inherently the calculations done by BLM are designed to figure out that concentration of $Cu(II)_{aq}$ that should be present in order to have the toxic effect of copper at the biotic ligand site. However, BLM then calculates the concentration of dissolved copper that should be present under those conditions, providing this as the result of the calculations. From there BLM follows a sequence to calculate WER for those waters.

This project is transitioning into project CP-0523, "Integrated Compliance Model for Predicting Fate and Effects of Copper in DoD Harbors," with support from the Environmental Security Technology Certification Program (ESTCP) with the objective of demonstrating an integrated modeling system that will provide an improved methodology for achieving compliance for copper in DoD harbors (i.e. development of TMDLs, site-specific WQS and WERs) in a manner consistent with the current regulatory framework recently released for copper in freshwater systems (EPA 2003). The proposed system will also provide a management tool for the optimization of efforts on source control, as it will be robust enough for forecasting effects on copper concentration and toxicity in the harbor as results of these efforts. This model will account for the natural characteristics of the harbor including transport, flushing, sediment exchange and complexation, to achieve more scientifically-based, cost-effective compliance. The integrated model will include the hydrodynamic transport and fate algorithm developed under CP-1156 as well as a copper toxicity parameter (i.e., BLM), for simultaneous evaluation of transport, fate, and potential effects of copper on a harbor-wide scale. Results of this demonstrated technology have the potential to significantly reduce control and treatment costs through more appropriate, site-specific WQS and discharge limits. Also, the development of copper toxicity parameters for the implementation of the BLM (Di Toro et al., 2001; Santore et al., 2001) in seawater should provide WQS that better represent the actual environmental characteristics of the harbor, and reduce requirements for costly empirical studies.

The fundamental innovation of this demonstration will be the integration of the fate and transport model with the BLM model, both being state-of-the-science products, to provide a complete framework for simultaneously evaluating transport, fate, and potential effects of copper on a harbor-wide scale. The requirement for this innovative model integration is increasingly driven by regulatory requirements to achieve compliance for point source discharges, and develop TMDLs and site-specific WQS. The integrated model will also provide a tool for the optimization of effluent control measures and further the development of the BLM in seawater.

The demonstration process involves three primary tasks including model calibration, model integration, and model validation. The overall process that we envision for the demonstration is shown in Figure 20. As TMDLs are developed in a whole harbor scale, the demonstrations will also be performed to that scale.

9 REFERENCES

Blake, A.C., D.B. Chadwick, A. Zirino and I. Rivera-Duarte, 2004. Spatial and temporal variations in copper speciation in San Diego Bay. Estuaries 27(3): 437-444.

Boyd T.J., D.M. Wolgast, I. Rivera-Duarte, O. Holm-Hansen, C.D. Hewes, A. Zirino, and D.B. Chadwick, 2005. Effects of dissolved and complexed copper on heterotrophic bacterial production in San Diego Bay. Microbial Ecology (in press).

Buffle, J.; R.S. Altman, M. Filella, A. Tessier, 1990. Complexation by natural heterogeneous compounds: Site-occupation distribution functions, a normalized description of metal complexation. Geochimica et Cosmochimica. Acta 54: 1535-1553.

Campbell, P.G.C., 1995. Interactions between trace metals and aquatic organisms: A critique to the free-ion activity model. In: Tessier, A.; Turner, D.R. (Eds.), *Metal Speciation and Bioavailability in Aquatic Systems*, John Wiley & Sons, pp: 45-102.

Chadwick, D.B., Zirino, A., Rivera-Duarte, I., Katz, C.N., and Blake, A.C., 2004. Modeling the mass balance and fate of copper in San Diego Bay. Limnology & Oceanography, 49: 355-366.

Chadwick, B., I. Rivera-Duarte, G. Rosen, T. Boyd, A. Zirino, L. Kear. 2005. Modeling copper speciation and toxicity in San Diego Bay (in prep).

Cheng, R.T., V. Casulli, and J.W. Gartner, 1993. Tidal, residual, intertidal mudflat (TRIM) model and its applications to San Francisco Bay, California, Estuarine, Coastal and Shelf Science, 36: 235-280.

DiToro, D.M., H.E. Allen, H.L. Bergman, J.S. Meyer, P.R. Paquin and R.C. Santore. 2001. A biotic ligand model of the acute toxicity of metals. I. Technical Basis. Environmental Toxicology and Chemistry, 20: 2383-2396.

Eriksen, R.S.; Mackey, D.J.; van Dam, R.; Nowak, B., 2001. Copper speciation and toxicity in Macquarie Harbour, Tasmania: an investigation using a copper ion selective electrode. Marine Chemistry, 74: 99-113.

Esser, B.K.; Volpe, A., 2002. At-sea high-resolution trace element mapping: San Diego Bay and its plume in the adjacent coastal ocean. Environmental Science & Technology, 36: 2826-2832.

Flegal A.R., G.J. Smith, G.A. Gill, S. Sañudo-Wilhelmy, and L.C.D. Anderson, 1991. Dissolved trace element cycles in the San Francisco Bay estuary. Marine Chemistry 36: 329-363.

Flegal, A.R., and S. Sañudo-Wilhelmy, 1993. Comparable levels of trace metal contamination in two semi-enclosed embayments: San Diego Bay and South San Francisco Bay. Environmental Science & Technology, 27: 1934-1936.

Johnson, H. D., J.G. Grovhoug, and A.O. Valkirs, 1998. Copper loading to U.S. Navy harbors. SPAWAR Systems Center Technical Document #3052.

Moffet, J.W.; Brand, L.E., 1996. Production of strong, extracellular Cu chelators by marine cyanobacteria in response to Cu stress. Limnology & Oceanography, 41: 388-395.

Morse J.W., B.J. Presley, R.J. Taylor, G. Benoit, and P. Santschi, 1993. Trace metal chemistry of Galveston Bay: water, sediments and biota. Marine Environmental Research 36: 1-37.

PRC, 1997. Report of copper loading to San Diego Bay, California, Report to California Regional Water Quality Control Board, San Diego Region, 14 May 1997.

Rivera-Duarte, I.; Zirino, A., 2004. Response of the Cu(II) ion selective electrode to Cu titration in artificial and natural shore seawater and in the measurement of the Cu complexation capacity. Environmental Science & Technology 38(11): 3139-3147.

Rivera-Duarte, I., G. Rosen, D. Lapota, D.B. Chadwick, L. Kear-Padilla, and A. Zirino, 2005. Copper toxicity to larval stages of three marine invertebrates and copper complexation capacity in San Diego Bay, California. Environmental Science & Technology 39(6): 1542-1546.

Rosen, G., I. Rivera-Duarte, L. Kear-Padilla, and D.B. Chadwick, 2005. Use of laboratory toxicity tests with bivalve and echinoderm embryos to evaluate the bioavailability of copper in San Diego Bay, California, USA. Environmental Toxicology and Chemistry 24(2): 415-422.

Sañudo-Wilhelmy, S.A., and A.R. Flegal, 1991. Trace element distribution in coastal waters along the US-Mexican boundary: relative contributions of natural processes vs. anthropogenic inputs. Marine Chemistry 33: 371-392

Schiff K. and D. Diehl, 2002. Assessment of trace metal emissions from antifouling paints during underwater cleaning events and passive leaching. International Congress on Marine Corrosion and Fouling, San Diego, California, 21-26 July 2002.

Seligman, P.F., A.O. Valkirs, J.S. Caso, I. Rivera-Duarte, and E. Haslbeck, 2001. Copper release rates from antifouling marine coatings and their relationship to loading and toxicity in San Diego Bay, California. In: Symposium on Pollution Prevention from Ships and Shipyards. Oceanology International 2001 Conference. Miami, Florida, April 4-5, 2001. M.A. Champ, Ed. pp. 64-81.

Seligman, P.F.; Zirino, A. Chemistry, Toxicity, and Bioavailability of Copper and its Relationship to Regulation in the Marine Environment, Technical Document 3044; Space and Naval Warfare Systems Center: San Diego, CA, 1998.

Shaffer M.M., S.R. Hoffman, J.T. Overdier, and D.E. Armstrong, 2004. Physical and kinetic speciation of copper and zinc in three geochemically contrasting marine estuaries. Environmental Science & Technology 2004, 38(14): 3810-3819.

Sunda, W.G.; Ferguson, R.L., 1983. Sensitivity of natural bacterial communities to additions of copper and to cupric ion activity: A bioassay of copper complexation in seawater. In: Wong, C.S; Boyle, E.A.; Bruland, K.W.; Burton, J.D.; Goldberg, E.D. (Eds.), *Trace Metals in Seawater*, Plenum Press, New York, pp: 871-891.

Sunda, W.G.; Guillard, R.L., 1976. The relationship between cupric ion activity and the toxicity of copper to phytoplankton. Journal of Marine Research 34: 511-529.

U.S. Environmental Protection Agency, 1994. *Interim Guidance on Determination and Use of Water-Effect Ratios for Metals.* EPA-823-B-94-001.

U.S. Environmental Protection Agency, 1996. *1995 Updates: Water Quality Criteria Documents for the Protection of Aquatic Life in Ambient Water.* EPA-820-B-96-001.

U.S. Environmental Protection Agency, 1999. Phase I uniform national discharge standards for vessels of the armed forces, technical development document. EPA 821-R-99-001.

U.S. Environmental Protection Agency, 2003. *Update of Ambient Water Quality Criteria for Copper.* EPA 822-R-03-026.

U.S. Environmental Protection Agency, 2002. National Recommended Water Quality Criteria: 2002. EPA-822-R-02-047.

Valkirs, A.O., Seligman, P.F., Haslbeck, E., and Caso, J.S., 2003. Measurement of copper release rates from antifouling paint under laboratory and in situ conditions: implications for loading estimation to marine water bodies. Marine Pollution Bulletin 46: 763-779.

Wang P.F., R.T. Cheng, K. Richter; E.S. Gross; D. Sutton; and J.W. Gartner, 1998. Modeling tidal hydrodynamics of San Diego Bay, California. Journal of the American Water Research Association, 34, 5: 1123-1140.

Wang, P.F., and Bart Chadwick, 1998. Dilution and Transport of Convention Center Effluent of Copper, Zinc and Silver in San Diego Bay. SPAWAR-SYSCEN draft report for the Port of San Diego.

Wang, P.F., Ron Gauthier and Jeff Grovhoug, 2002. Simulation of Fate and Transport of Antifouling Biocides in San Diego Bay. SSC-SD draft report to NAVSEA.

Wang, P.F., B. Chadwick, I. Rivera-Duarte, M. Brand, and A. Zirino. 2005. Application of the two-dimensional Tidal Residual Intertidal Mudflat (TRIM2D) model to the transport, speciation and fate of copper in a San Diego Bay (in prep).

Wei L., J.R. Donat, G. Fones, and B.A. Ahner, 2003. Interactions between Cd, Cu, and Zn influence particulate phytochelatin concentrations in marine phytoplankton: laboratory results and preliminary field data. Environmental Science & Technology 37: 3609-3618

Woodward-Clyde, 1996. PAH waste load determinations for San Diego Bay. Report to the California Regional Water Quality Control Board, San Diego Region and San Diego Bay Interagency Water Quality Panel.

Zirino, A., S. Lieberman and C. Clavell, 1978. Measurement of Cu and Zn in San Diego Bay by automated anodic stripping voltammetry. Environmental Science & Technology, 12: 73-79.

Zirino, A.; Seligman, P.F. Copper Chemistry, Toxicity, and Bioavailability and Its Relationship to Regulation in the Marine Environment, Technical Document 3140; Space and Naval Warfare Systems Center: San Diego, CA, 2002.

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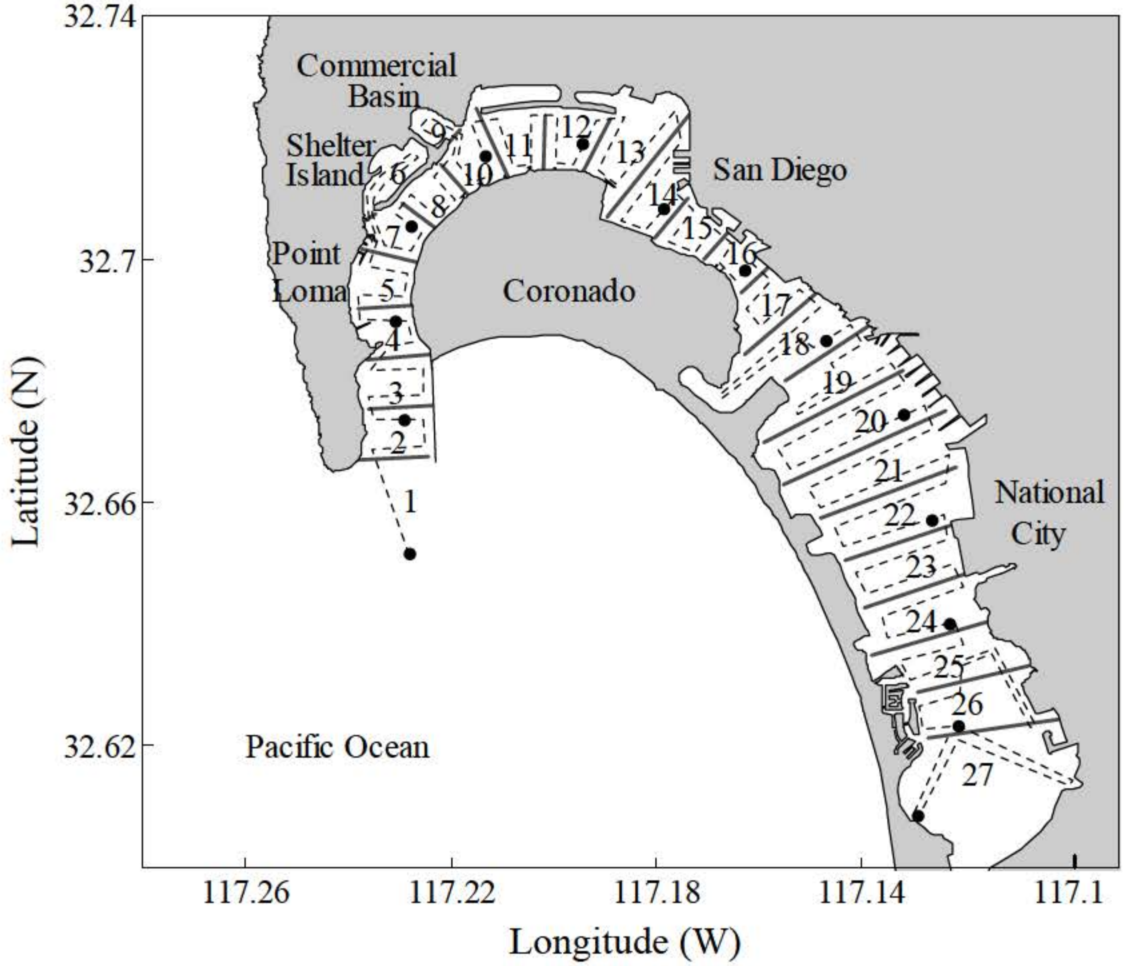

Figure 1. Boxes, sampling transect, depth profile stations and enclosed bodies of water studied in San Diego Bay.

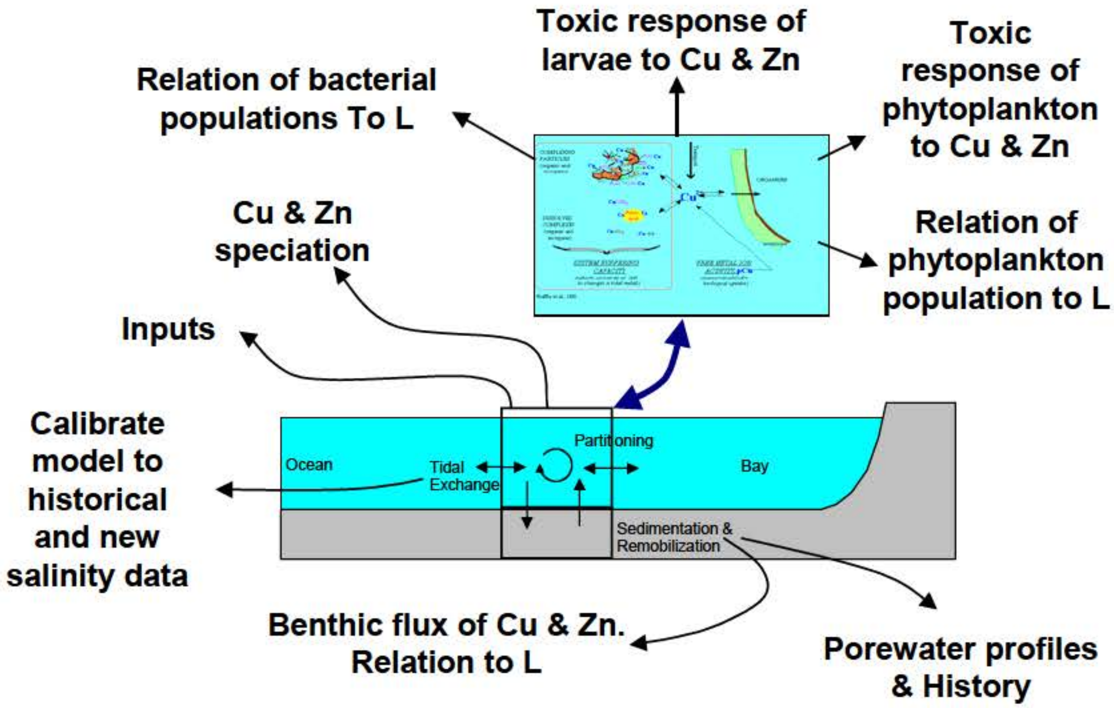

Figure 2. Diagram of the components of the multidisciplinary effort. The top box represents the Free Ion Model (Figure 3) and the chemical characteristics measured in this effort. Similarly, the bottom box represents the physical parameters measured in each of the boxes of the one-dimensional model.

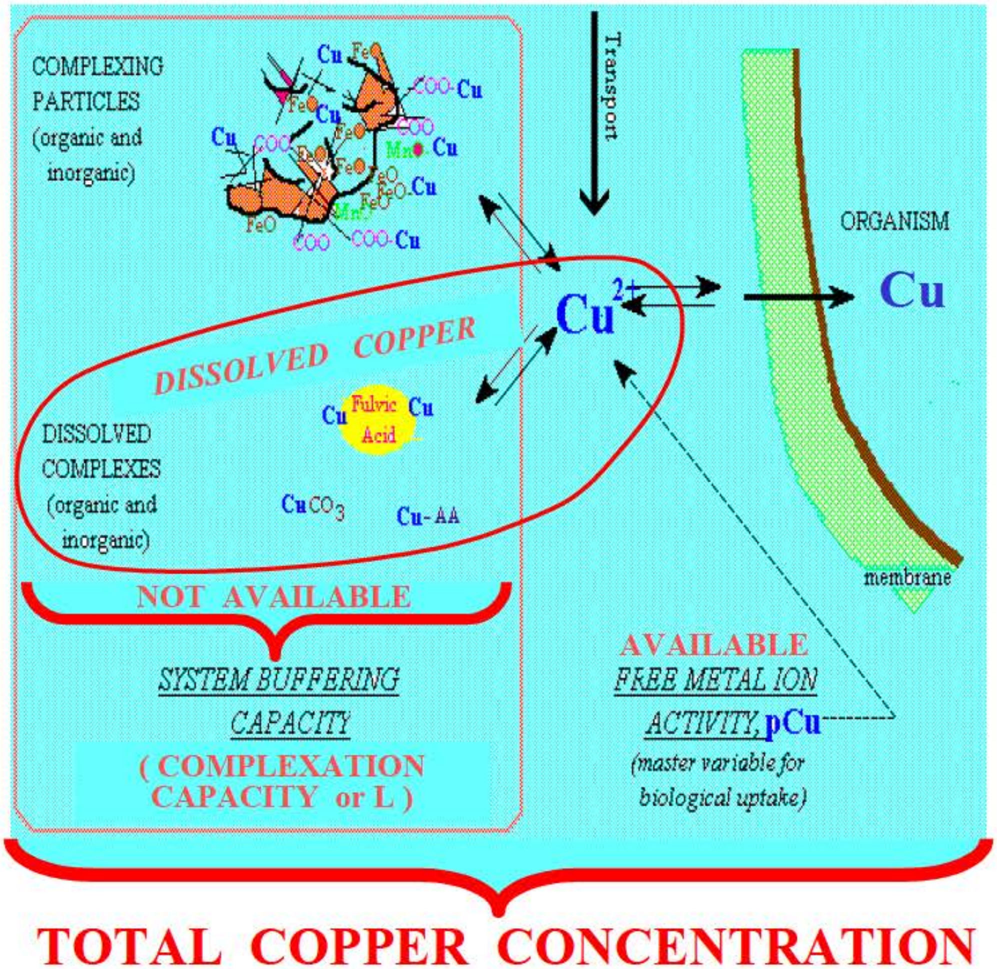

Figure 3. Free ion activity model of Buffle et al (1990). The figure is modified from the original to indicate the total and dissolved fractions of copper, the free copper ion that is available to the organisms, as well as the fraction that defines the natural complexation capacity of the water.

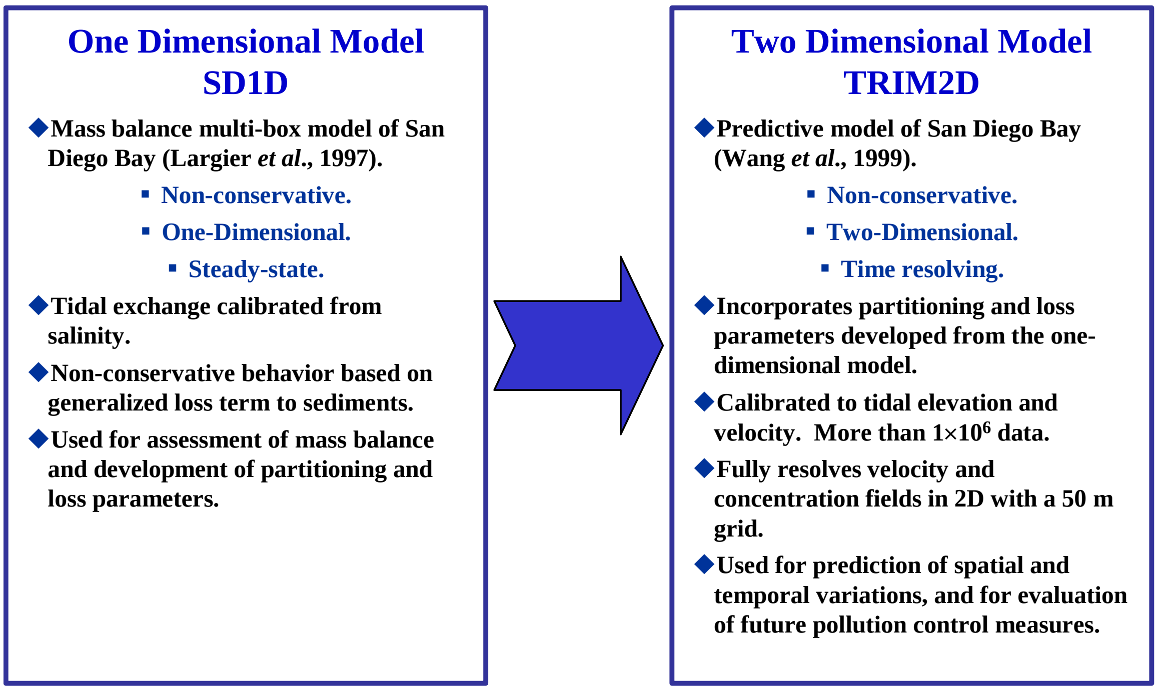

Figure 4. Graphical explanation of the models used in this effort. The one-dimensional model, SD-1D, was used to simulate steady-state conditions at each box and for the assessment of partitioning and loss parameters. These parameters were then feed into the two-dimensional model, TRIM-2D, for the resolution of spatial and temporal variations, and for its use as predictive tool for the management of the sources of copper to San Diego Bay.

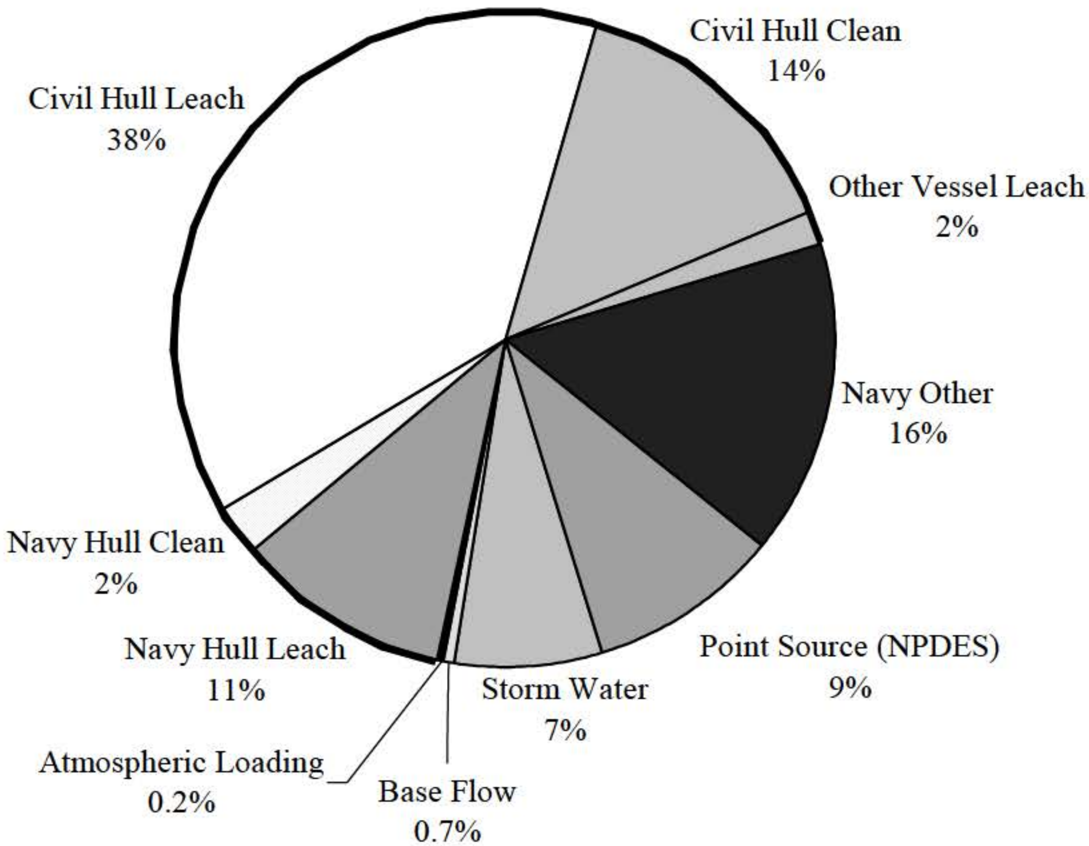

Figure 5. Inputs of copper to San Diego Bay. The data was modified from Johnson et al. (1998) and PRC (1997). It was updated to account for recent improvements in estimates for various input rates, and to incorporate estimates for particulate copper (Chadwick et al., 2004). Those inputs that are related to antifouling paints are indicated by the bold outline, and are 65% to the total inputs to the bay.

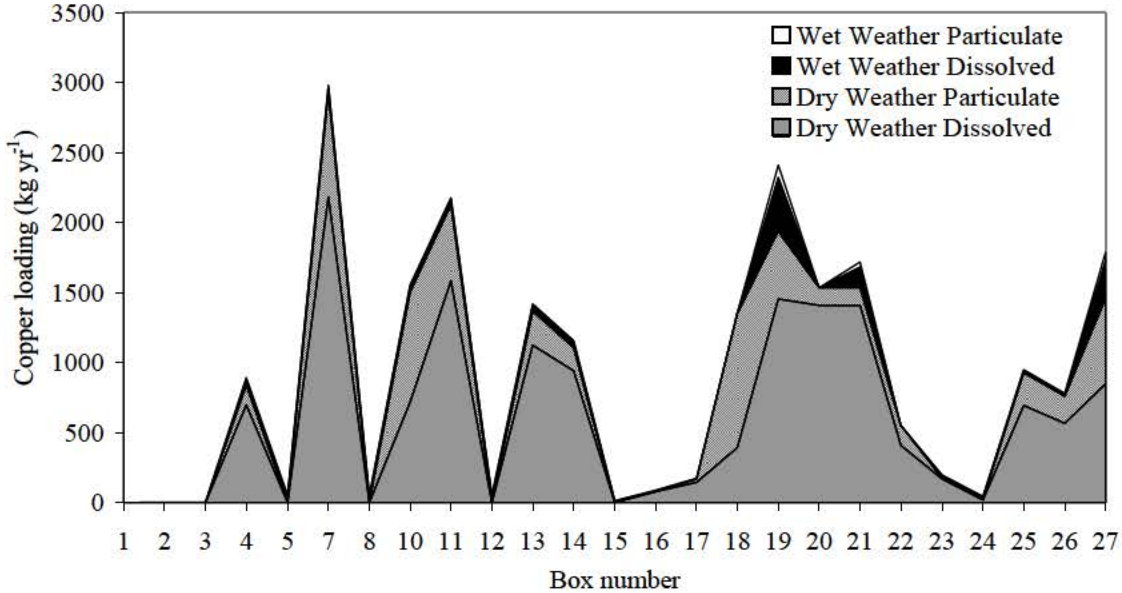

Figure 6. Distribution of copper sources within San Diego Bay. While this is not shown in the figure, the northern part of the bay (boxes 1 to 15) is dominated by leaching from antifouling paints in pleasure craft, and the southern part of the bay (boxes 17 to 27) is dominated by leaching from military ships hulls.

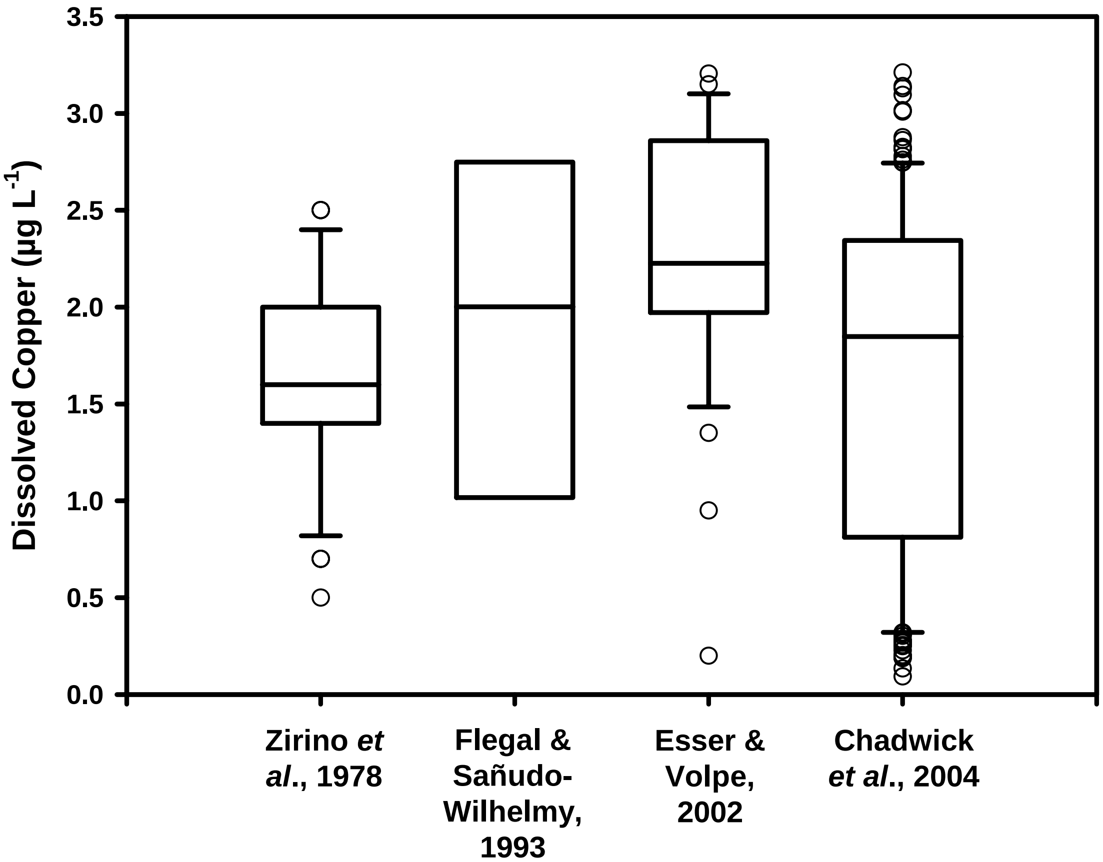

Figure 7. Historical trend in dissolved (≤0.45 µm) copper concentration (µg L^{-1}) in San Diego Bay. Each box indicates the median and the 25th and 75th percentile, the bars below and above show the 10th and 90th percentiles, and outlying data is represented with closed circles. The data is from Zirino et al. (1978), Flegal and Sañudo-Wilhelmy (1993), Esser and Volpe (2002) and dissolved copper concentrations measured during our six sampling campaigns (Chadwick et al, 2004). Note that the concentrations from Zirino et al. (1978) are from unfiltered samples and measured by differential pulse anodic stripping voltammetry, but our experience indicates that these measurements are more representative of dissolved copper concentrations.

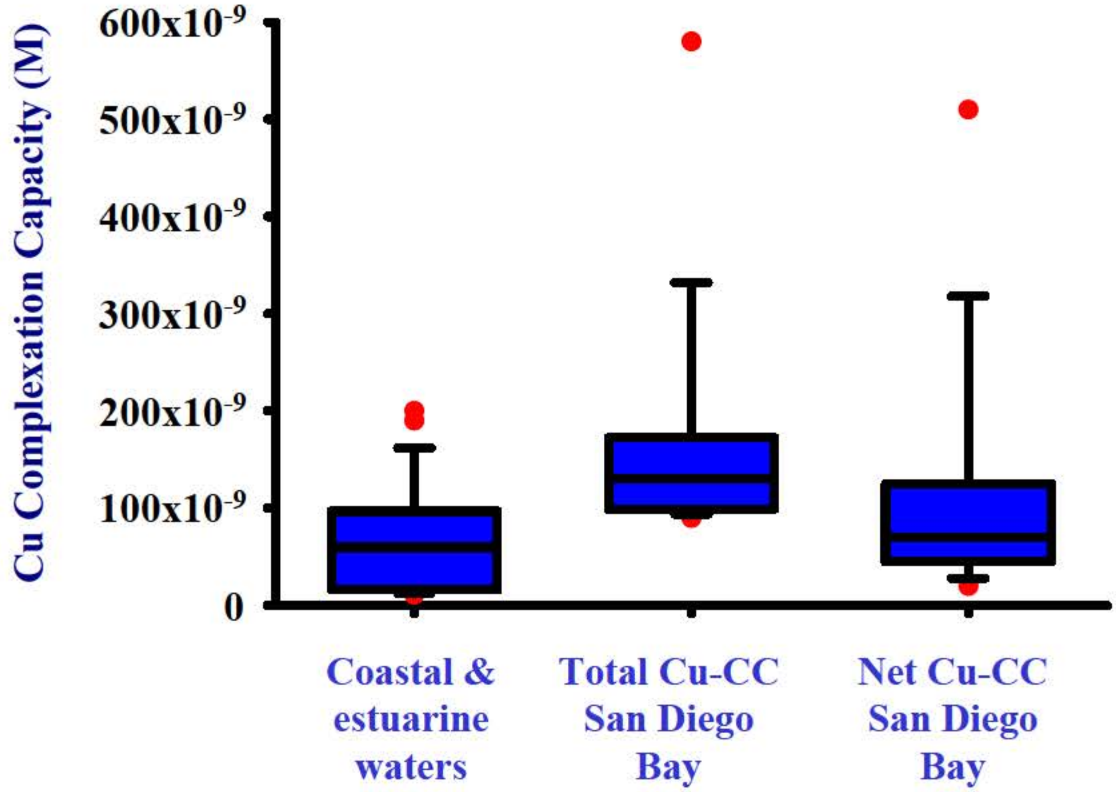

Figure 8. Comparison on the natural copper buffering capacity, or complexation capacity in coastal waters. The range for coastal and estuarine waters is from references that used a suite of techniques, and the values are the sum of the ligands present ($L_1+L_2+\ldots+L_i$). The ranges for San Diego Bay were measured with the copper ion selective electrode and represent the total measured and the net after the initial copper concentration was subtracted.

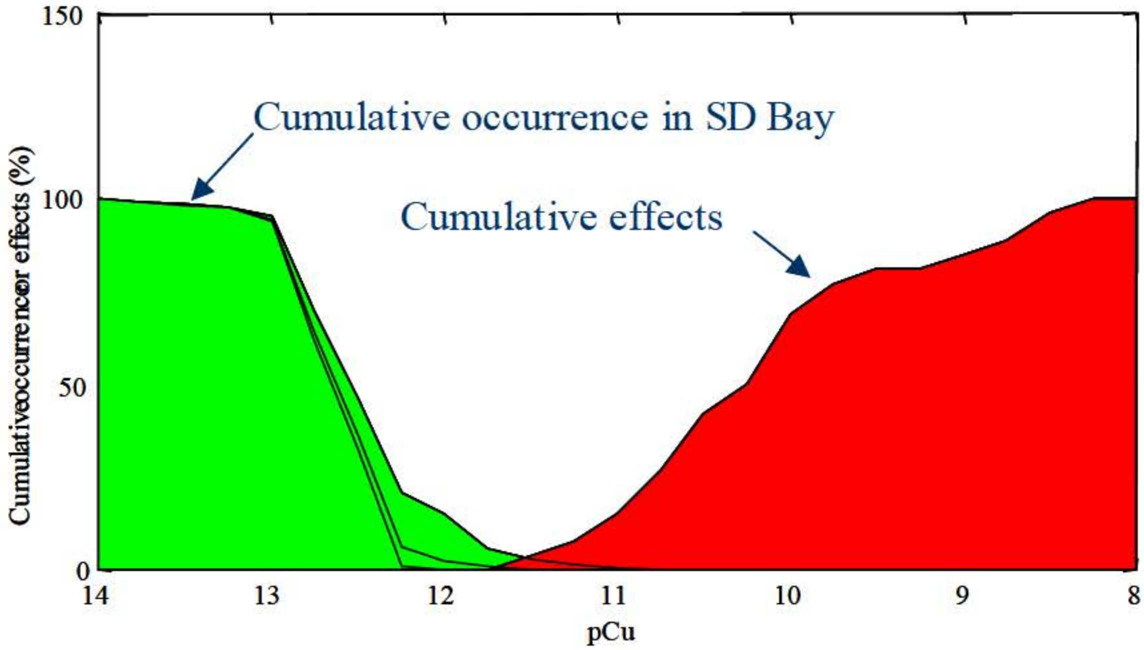

Figure 9. Cumulative occurrence and effects of $Cu(II)_{aq}$ in San Diego Bay. The concentration of free copper ion ($Cu(II)_{aq}$, x-axis) is given as pCu, or $-\log [Cu(II)_{aq}]$, and it is in reverse order as it indicates an increase in concentration. Free copper ion concentrations in San Diego Bay ranged from pCu 14 to pCu 11.5. Cumulative deleterious effects start occurring at a pCu of about 11.

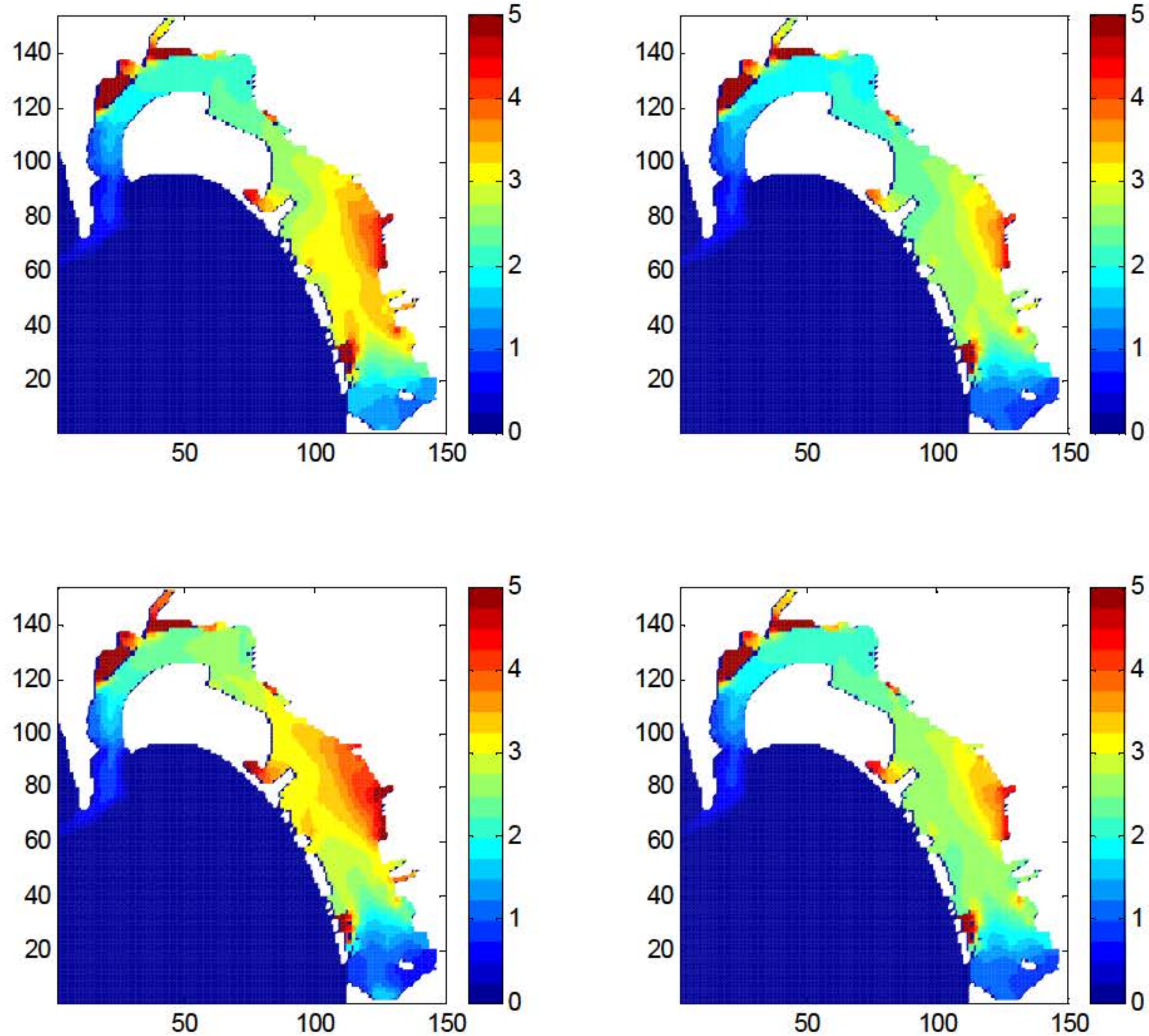

Figure 10. TRIM-2D simulations of the total copper concentration in San Diego Bay (μg/L). Simulations are based on conditions characteristic of the August 2000 (upper left), January 2001 (lower left), May 2001 (upper right), and September 2001 (lower right) annual cycle.

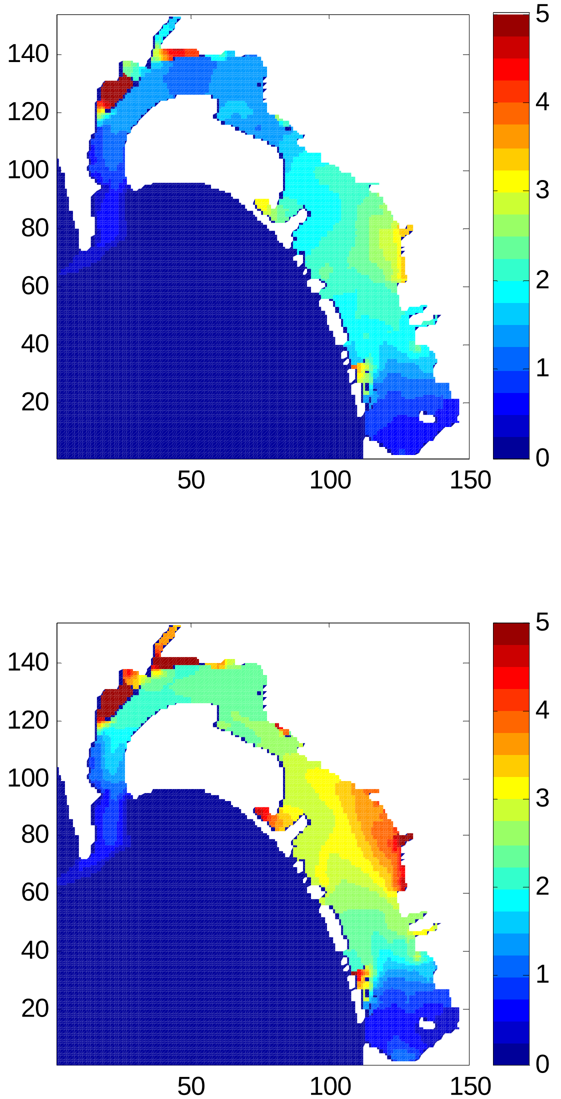

Figure 11. TRIM-2D simulations of the dissolved copper concentration in San Diego Bay (μg/L). Simulations are based on conditions characteristic of the August 2000 (upper left), January 2001 (lower left), May 2001 (upper right), and September 2001 (lower right) annual cycle.

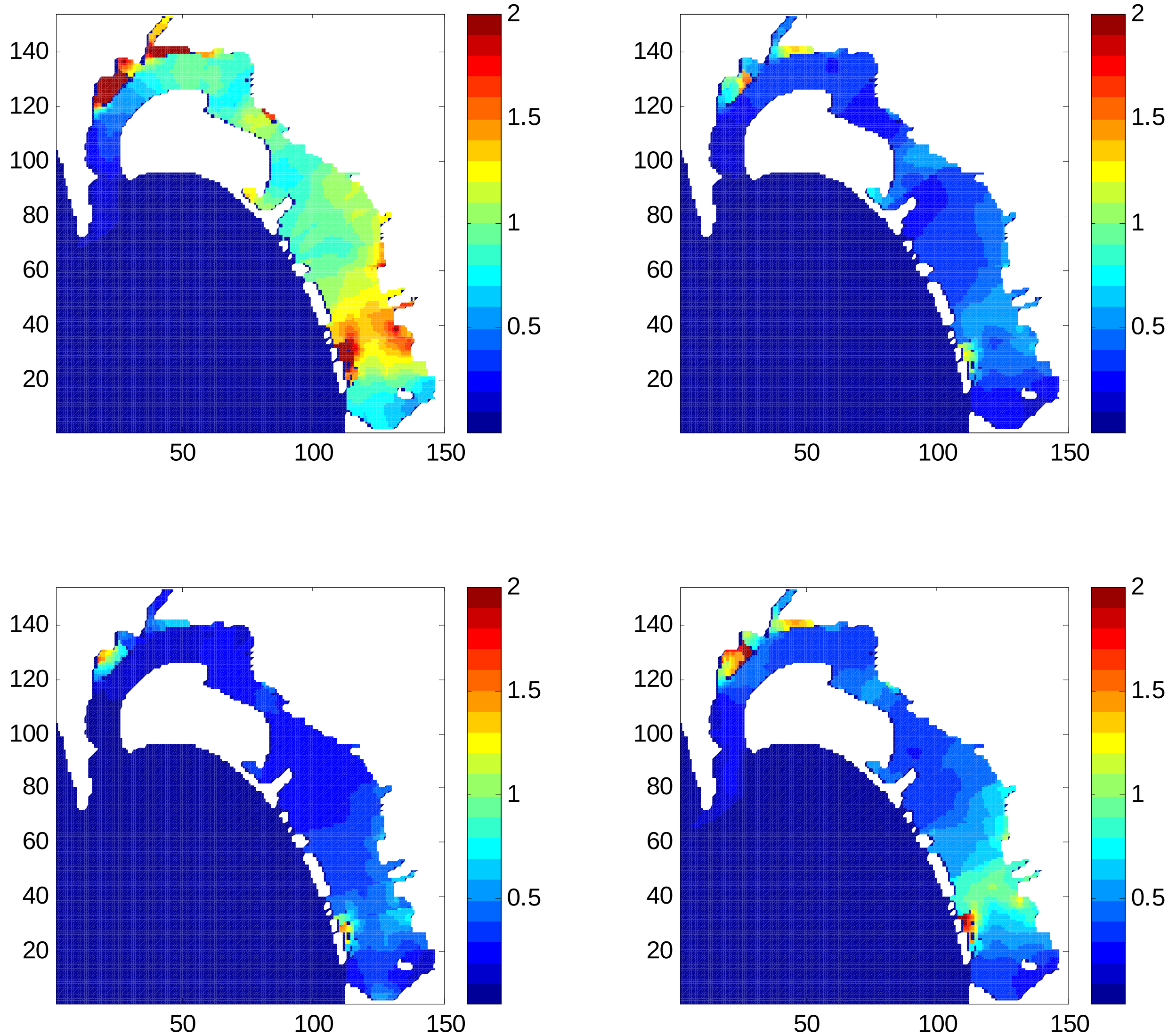

Figure 12. TRIM-2D simulations of the particulate copper concentration in San Diego Bay (μg/L). Simulations are based on conditions characteristic of the August 2000 (upper left), January 2001 (lower left), May 2001 (upper right), and September 2001 (lower right) annual cycle.

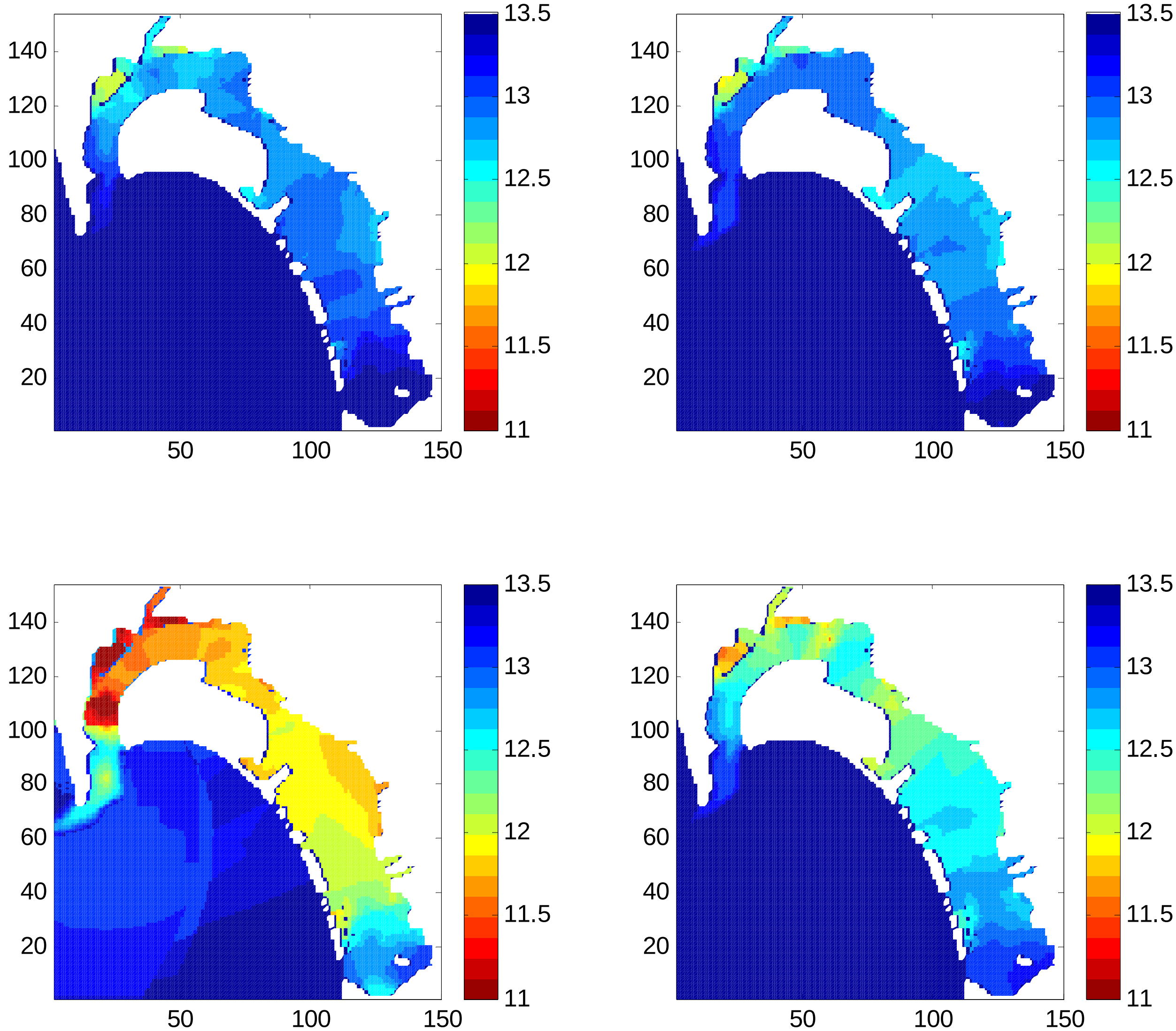

Figure 13. TRIM-2D simulations of the free copper concentration in San Diego Bay (pCu). Simulations are based on conditions characteristic of the August 2000 (upper left), January 2001 (lower left), May 2001 (upper right), and September 2001 (lower right) annual cycle.

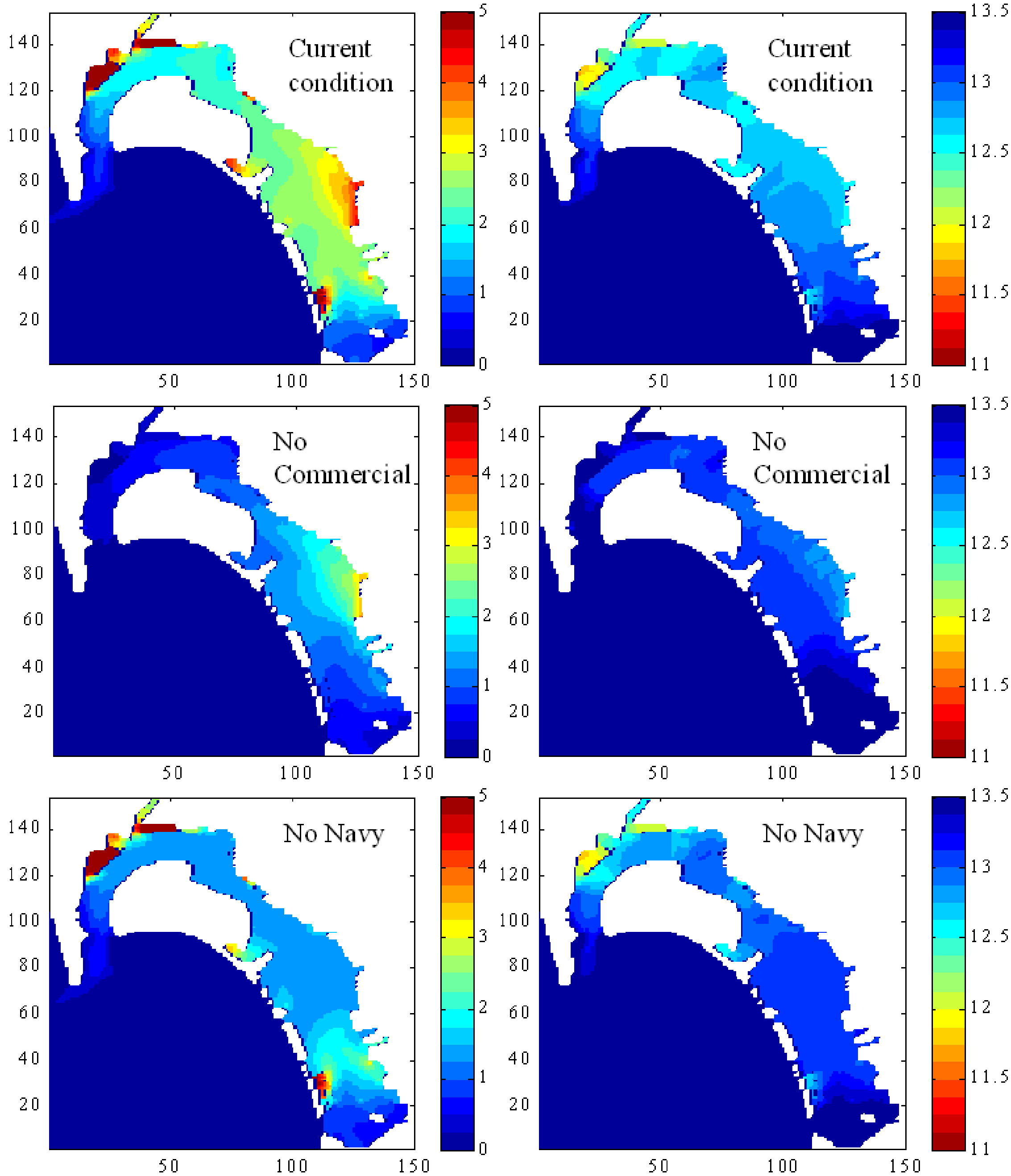

Figure 14. Modeled results for dissolved copper (left panels) and free copper (right panels) to hypothetical changes in copper loading including current condition (top), predicted distribution with no commercial loading (mid), and predicted distribution with no Navy loading (bottom).

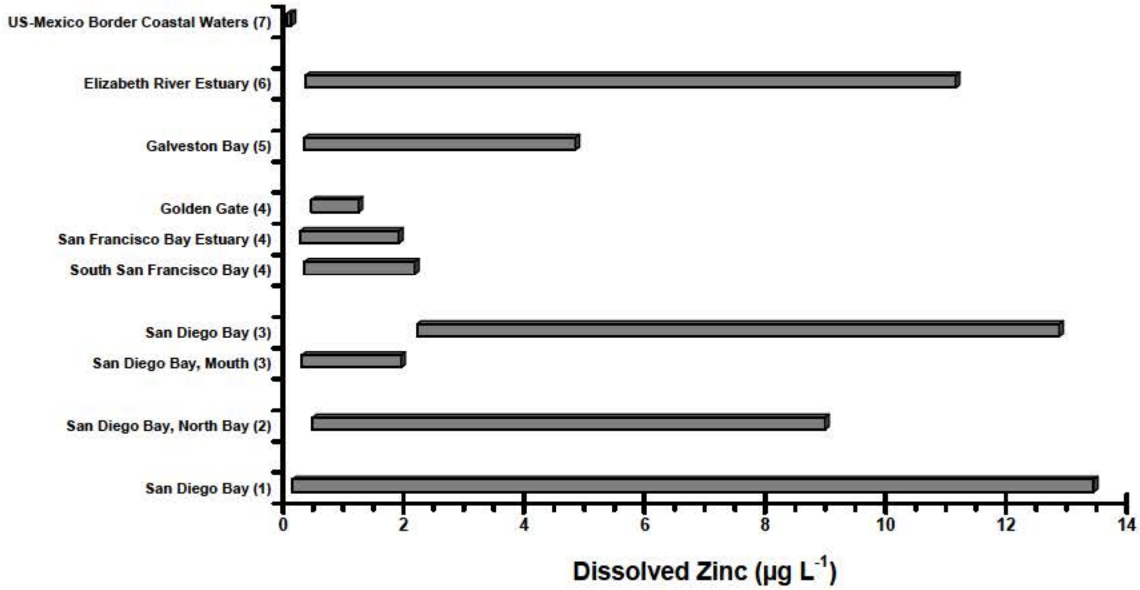

Figure 15. Concentrations of dissolved zinc measured in San Diego Bay and other coastal embayments. Total zinc concentrations are reported for the U.S.-Mexico border. The number in parenthesis indicate the reference source as follows: (1) this work, (2) Esser and Volpe, 2002, (3) Shaffer et al., 2004, (4) Flegal et al., 1991, (5) Morse et al., 1993, (6) Wei et al., 2003, and (7) Sañudo-Wilhelmy and Flegal, 1991.

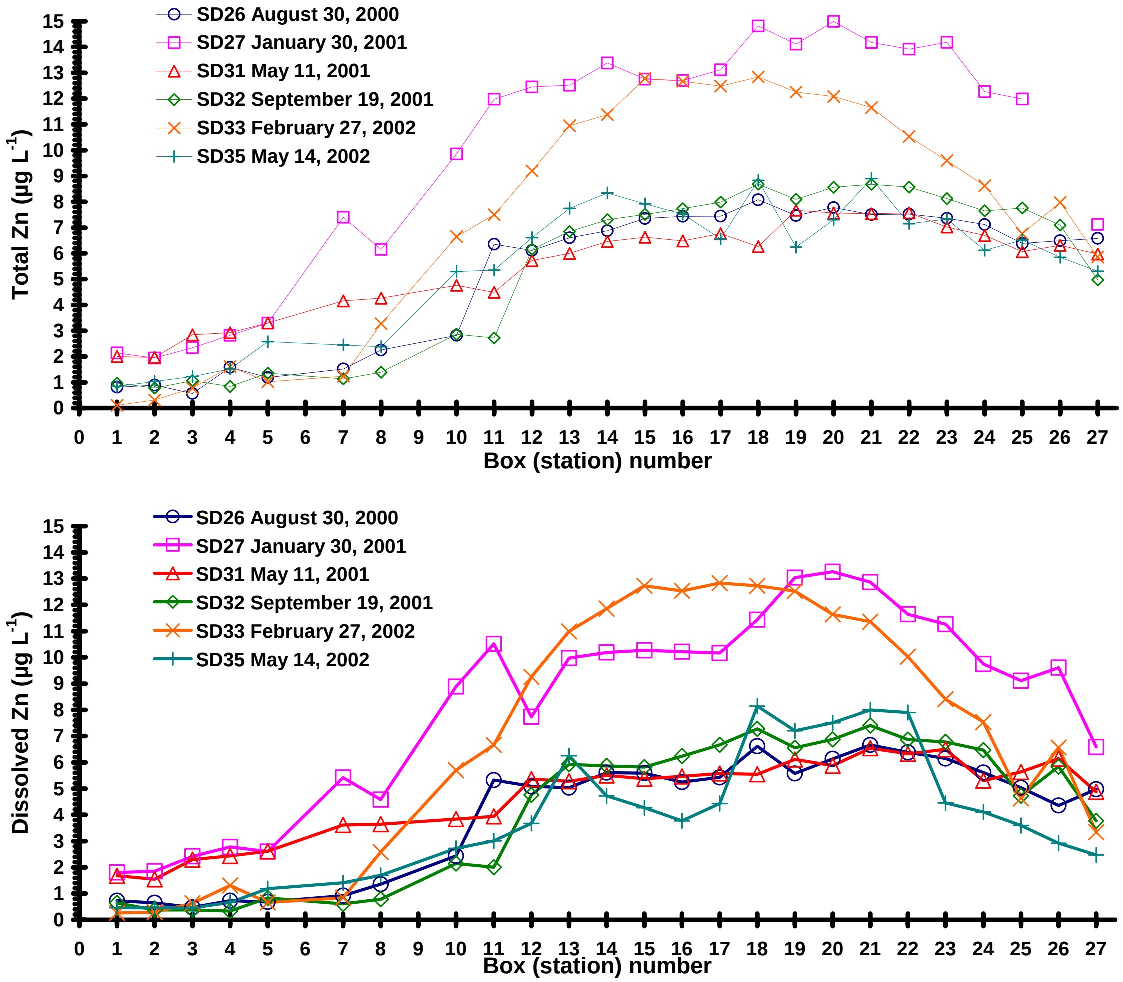

Figure 16. Spatial distributions of total (i.e., unfiltered) and dissolved (i.e., 0.45µm) zinc in San Diego Bay. The abscissa indicates the box number, and does not include data for either Shelter Island (box 6) or Commercial Basin (box 9).

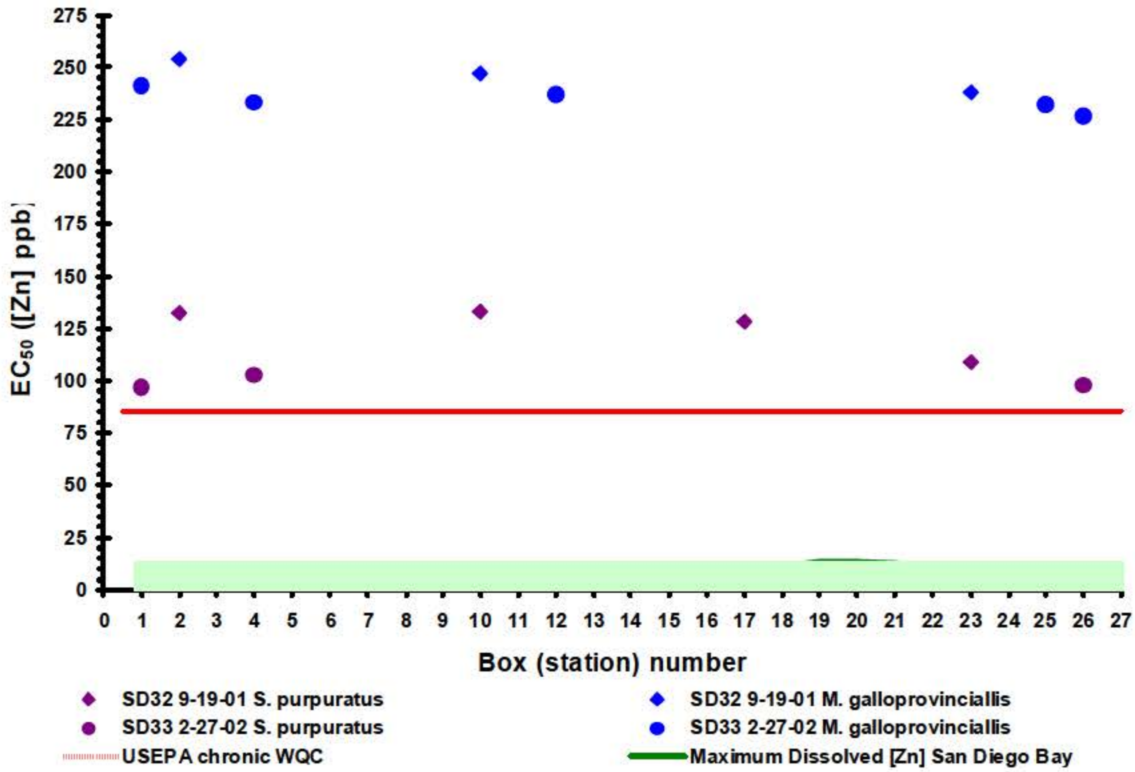

Figure 17. Spatial comparison of the maximum concentrations of dissolved zinc (µg L^{-1}) and larval-development EC_{50} measured in San Diego Bay, with the USEPA WQC (85 µg L^{-1}) for aquatic life in seawater (EPA 2002). The difference in the values indicates that waters in San Diego Bay are healthy with respect to zinc concentrations.

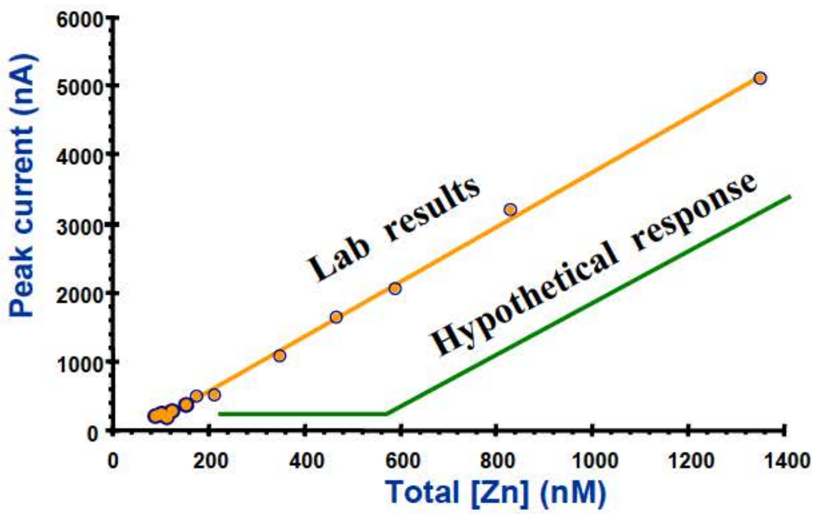

Figure 18. Comparison of lab results of analysis of zinc speciation by anodic stripping voltammetry with a hanging mercury electrode, and the hypothetical response when zinc is complexed and free zinc ion is present at undetectable concentrations. The linear increase in the signal with the additions of zincs indicate that zinc is present as free ion throughout the titration.

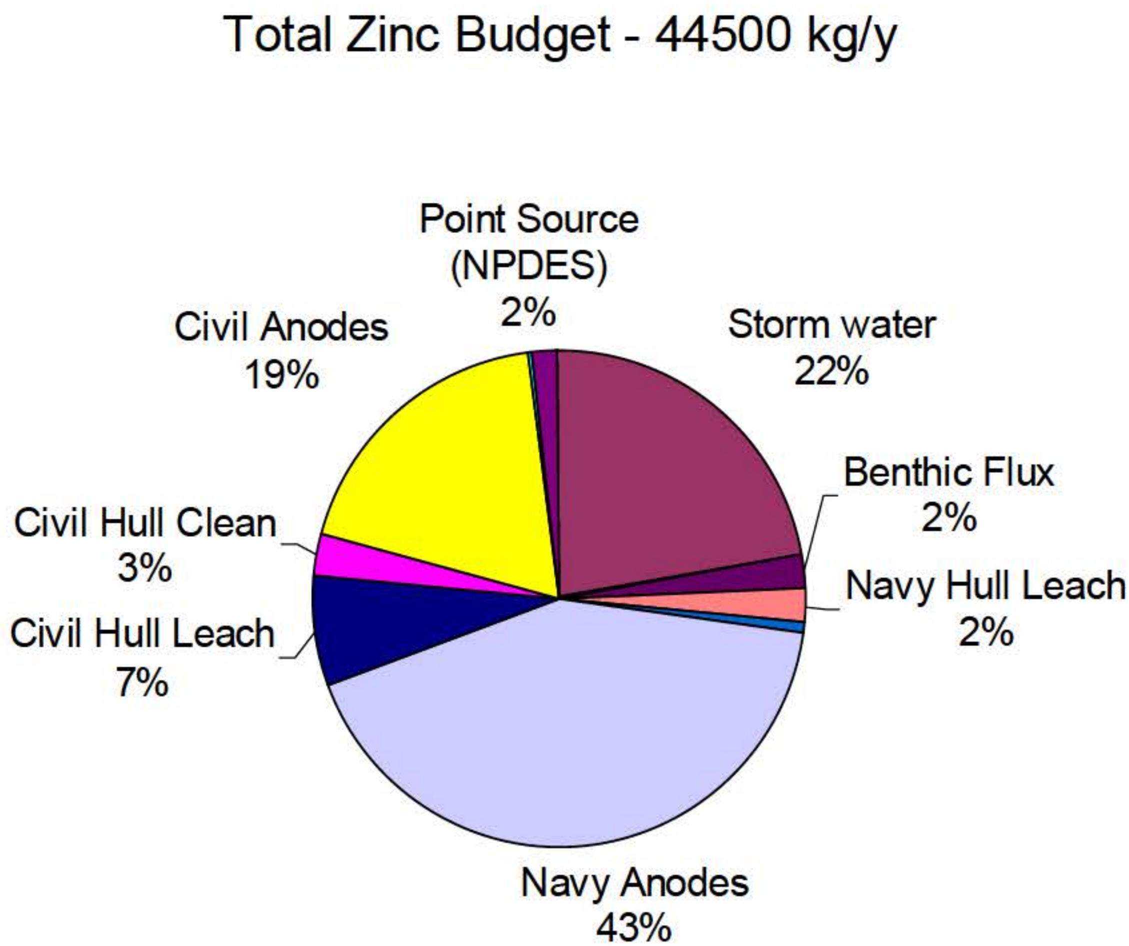

Figure 19. Inputs of zinc to San Diego Bay.

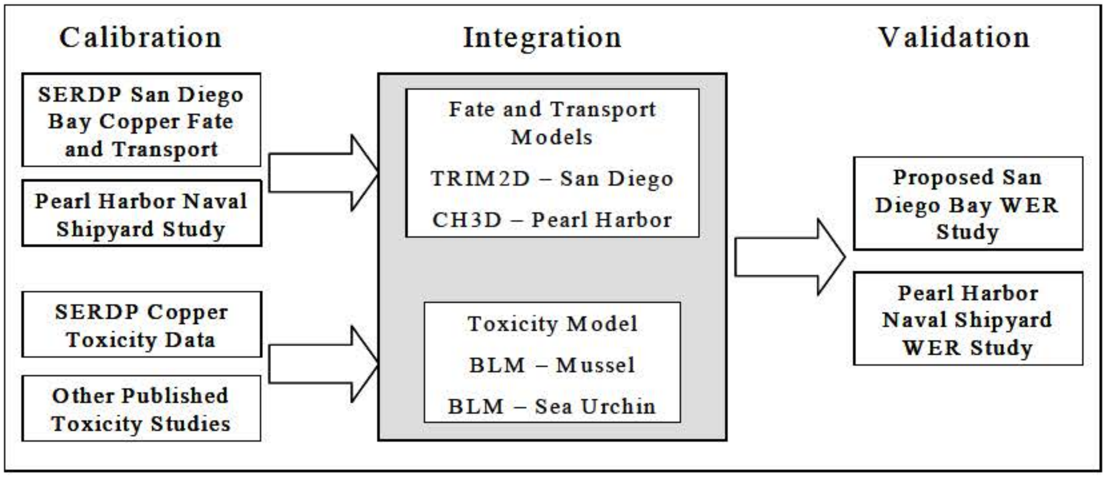

Figure 20. Calibration, integration and validation process of the integrated transport and toxicity models for copper.

APPENDIX A: SUPPORTING DATA

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SD26: August 2000

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Parameter	Time	Residence Time	In Situ Temp	In Situ pH	In Situ Light Trans. @ 670 nm	In Situ UVF	In Situ Salinity	Density	In Situ Oxygen	In Situ Oxygen
Data Units	Day of August 00	(days)	(^{o}C)	(NBS)	(%)	(ug/L DFM)	(psu)	(sigma-t)	(mg/L)	(% sat.)
Data Type		model	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ
Data Source	SPAWAR	SD1D	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments										
Sample ID										
SD26-01	30.3614769	0.00	17.546	8.077	82.20	0.69	33.56	24.28	6.21	113.75
SD26-02	30.3721012	0.05	18.038	8.072	76.08	2.49	33.58	24.18	6.04	111.66
SD26-03	30.3864978	0.15	18.057	8.068	74.32	2.17	33.57	24.16	5.96	110.22
SD26-04	30.3977399	0.36	17.805	8.064	74.73	3.44	33.58	24.23	6.03	111.03
SD26-05	30.4086918	0.74	18.686	8.058	68.99	6.30	33.65	24.06	5.74	107.49
SD26-06	30.4262511	NS	20.871	8.019	58.85	17.30	33.82	23.63	4.97	96.99
SD26-07	30.4432431	1.18	18.083	8.049	69.82	3.69	33.61	24.18	6.02	111.43
SD26-08	30.4528114	1.63	18.171	8.057	68.85	6.41	33.60	24.16	5.94	110.13
SD26-09	30.4644337	NS	21.718	7.987	54.35	19.05	33.94	23.49	4.57	90.65
SD26-10	30.4781085	2.30	19.558	8.036	59.79	9.70	33.72	23.90	5.58	106.18
SD26-11	30.4897727	3.19	20.089	8.031	56.01	12.37	33.76	23.79	5.32	102.39
SD26-12	30.5024754	4.17	21.548	8.001	55.42	19.81	33.96	23.55	4.84	95.74
SD26-13	30.5159179	5.79	22.176	7.983	55.13	21.39	34.04	23.44	4.63	92.70
SD26-14	30.5306147	7.47	22.294	7.973	59.41	22.62	34.05	23.42	4.59	92.18
SD26-15	30.5432927	8.44	22.483	7.960	55.23	24.18	34.10	23.40	4.45	89.69
SD26-16	30.5525084	9.33	22.615	7.958	60.14	24.65	34.12	23.38	4.45	89.87
SD26-17	30.5622384	10.71	22.848	7.956	60.92	25.44	34.16	23.34	4.44	90.13
SD26-18	30.5807735	12.60	23.449	7.937	61.02	27.60	34.29	23.27	4.29	87.96
SD26-19	30.6031640	14.99	23.471	7.943	59.34	26.47	34.32	23.28	4.37	89.59
SD26-20	30.6261605	17.83	24.099	7.936	61.56	30.21	34.60	23.31	4.26	88.50
SD26-21	30.6535808	20.49	24.422	7.933	63.26	32.05	34.76	23.34	4.22	88.21
SD26-22	30.6846970	22.79	24.502	7.934	63.41	33.13	34.83	23.37	4.26	89.24
SD26-23	30.7062864	25.19	24.549	7.936	60.00	33.98	35.02	23.49	4.30	90.27
SD26-24	30.7250519	27.63	24.518	7.939	58.43	35.76	35.18	23.63	4.34	91.08
SD26-25	30.7470888	30.06	24.759	7.942	53.38	36.87	35.39	23.71	4.30	90.78
SD26-26	30.7575005	33.57	24.953	7.933	44.04	37.49	35.56	23.78	4.14	87.84
SD26-27	30.7808031	37.64	24.752	7.922	36.04	38.22	35.86	24.07	4.19	88.77

Parameter	Flow Thru UVF	Flow Thru Chl-a	Flow Thru Cu Jalpaite ISE	Flow Thru Cu Chalcog. ISE	Flow Thru pH	pH2 TMA Cu	pH8 TMA Cu	total Cu	diss. Cu	total Zn	diss. Zn	TSS
Data Units	(volts)	(ug/L)	(pCu)	(pCu)	(NBS)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(mg/L)
Data Type	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Lab	Lab	Lab	Lab	Lab
Data Source	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments												
Sample ID												
SD26-01	0.226	1.043	12.97	11.45	8.250	0.4	0.4	0.4	0.3	0.81	0.73	0.36
SD26-02	0.226	1.158	12.98	11.45	8.241	0.2	0.2	0.4	0.3	0.89	0.65	1.06
SD26-03	0.226	1.200	12.99	11.46	8.232	0.3	0.1	0.3	0.2	0.56	0.47	1.00
SD26-04	0.227	1.152	13.10	11.46	8.234	0.1	0.0	0.7	0.4	1.6	0.73	1.16
SD26-05	0.227	1.195	13.08	11.49	8.216	0.3	0.1	0.5	0.3	1.2	0.68	1.28
SD26-06	0.225	2.130	12.82	11.54	8.174	0.9	0.4	4.8	2.4	12.2	7.8	2.28
SD26-07	0.228	1.211	12.69	11.54	8.213	2.0	1.8	0.7	0.4	1.5	0.92	1.48
SD26-08	0.228	1.213	12.87	11.49	8.219	0.9	0.6	0.9	0.4	2.3	1.4	1.62
SD26-09	0.226	1.496	12.82	11.60	8.142	1.1	0.4	3.8	2.4	9.4	6.7	2.74
SD26-10	0.230	1.293	12.87	11.57	8.195	1.3	0.4	1.2	0.7	2.8	2.4	2.40
SD26-11	0.230	1.341	12.93	11.57	8.185	0.8	NS	2.5	1.5	6.4	5.3	3.20
SD26-12	0.229	1.382	12.98	11.66	8.150	1.5	NS	2.0	1.1	6.1	5.1	2.68
SD26-13	0.228	1.403	12.97	11.70	8.135	1.6	NS	2.2	1.3	6.6	5.0	2.44
SD26-14	0.228	1.366	12.92	11.72	8.121	1.7	1.0	2.5	1.4	6.9	5.6	1.52
SD26-15	0.229	1.307	12.95	11.75	8.112	1.9	0.9	3.0	1.9	7.4	5.6	3.60
SD26-16	0.228	1.255	12.94	11.76	8.112	2.0	0.8	2.8	1.5	7.4	5.2	2.24
SD26-17	0.227	1.330	12.92	11.77	8.109	2.0	1.1	2.6	1.9	7.4	5.4	1.60
SD26-18	0.226	1.781	12.90	11.83	8.092	2.0	1.8	2.5	1.8	8.1	6.6	1.46
SD26-19	0.227	1.547	12.95	11.89	8.101	2.6	1.7	2.7	1.8	7.5	5.6	1.96
SD26-20	0.226	1.737	13.01	11.98	8.098	2.7	1.6	3.0	2.1	7.8	6.1	1.62
SD26-21	0.226	1.846	13.00	12.04	8.101	3.3	1.4	3.2	2.4	7.5	6.7	1.59
SD26-22	0.226	2.005	12.87	12.07	8.107	2.5	1.7	3.3	2.6	7.5	6.4	1.22
SD26-23	0.227	2.085	13.01	12.15	8.109	NS	1.5	3.2	2.3	7.4	6.2	2.02
SD26-24	0.227	2.273	13.08	12.20	8.117	2.2	1.4	2.9	2.1	7.1	5.6	2.08
SD26-25	0.229	2.523	13.04	12.23	8.117	2.5	1.5	3.1	2.2	6.4	5.0	2.68
SD26-26	0.231	2.585	13.06	12.31	8.115	2.8	1.5	3.1	2.1	6.5	4.4	3.31
SD26-27	0.234	2.879	13.16	12.37	8.106	2.3	1.6	3.1	2.2	6.6	5.0	4.24

Parameter	Bacterial Production	DOC	Total Alkalinity	Chloro-phyll	Phaeo-pigments	Bact. Abund.	Cyano Abund.	NO_3	PO_4	Si	NO_2	NH_3
Data Units	(ugC/L/d)	(mg/L)	um kg^{-1}	(mg m^{-3})	(mg m^{-3})	(ml^{-1})	(ml^{-1})	(uM)	(uM)	(uM)	(uM)	(uM)
Data Type	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
Data Source	NRL Boyd	NRL Boyd	UABC Ayon	SIO Holm-Hansen	SIO Holm-Hansen	SIO Holm-Hansen	SIO Holm-Hansen	SIO ODF	SIO ODF	SIO ODF	SIO ODF	SIO ODF
Comments												
Sample ID												
SD26-01	8.45	2.18	2224	0.88	0.46	1479250	25077	0.26	0.44	3.5	0.03	0.37
SD26-02	9.64	NaN	2241	1.04	0.58	2035485	38175	0.31	0.52	4.8	0.06	0.85
SD26-03	10.97	1.91	2208	1.05	0.73	1205175	48437	0.48	0.54	4.1	0.06	1.04
SD26-04	10.93	1.80	NS	1.01	0.68	1510573	27092	0.31	0.52	5.1	0.06	1
SD26-05	12.71	1.92	2235	1.19	0.75	1280704	24218	0.48	0.63	6.4	0.07	1.71
SD26-06	14.44	1.81	2233	2.00	1.09	1866424	9473	0.47	0.85	8.6	0.09	2.67
SD26-07	12.52	1.77	2241	1.18	0.81	NS	NS	1.21	0.64	5.5	0.08	1.58
SD26-08	11.80	1.78	2252	1.21	0.74	1797363	23397	0.28	0.57	4.8	0.06	1.31
SD26-09	15.67	2.07	2230	2.02	1.07	1467883	9031	0.92	1.1	11.8	0.15	4.54
SD26-10	11.95	1.75	2244	1.42	0.86	1732084	28851	0.65	0.75	7.1	0.08	2.43
SD26-11	13.18	1.77	2227	1.46	0.90	2132864	20935	0.42	0.76	7.3	0.07	7.48
SD26-12	11.06	2.09	2263	1.59	0.93	1912846	8210	0.59	1.03	10.8	0.1	4.29
SD26-13	10.72	2.11	2244	1.46	0.93	NS	NS	0.58	1.13	11.6	0.1	5.19
SD26-14	10.45	2.02	2301	1.51	0.91	1643570	3284	1.06	1.15	12.3	0.12	5.7
SD26-15	11.75	2.15	2236	1.27	1.01	2486177	3694	0.63	1.24	13.1	0.12	4.79
SD26-16	11.48	2.26	2252	1.29	0.91	1454449	5374	0.85	1.24	12.7	0.12	4.73
SD26-17	10.14	NS	2291	1.34	0.97	2466175	1642	0.59	1.09	11.1	0.11	4.46
SD26-18	11.04	NS	2272	1.74	1.17	2324969	6157	0.65	1.34	14.7	0.13	5.67
SD26-19	10.49	2.60	2283	1.42	1.19	NS	NS	0.97	1.39	14.5	0.14	5.86
SD26-20	12.03	NS	NS	1.60	1.42	1704321	2873	0.64	1.42	15.9	0.14	5.21
SD26-21	8.34	2.54	2272	1.69	1.53	NS	NS	0.9	1.44	16.3	0.14	4.77
SD26-22	8.97	2.69	2308	1.97	1.73	1093524	2052	0.65	1.51	20.7	0.14	4.14
SD26-23	15.12	2.73	2314	1.97	2.00	2366018	821	0.55	1.62	20.1	0.14	3.73
SD26-24	18.58	2.33	2306	2.33	1.94	2366167	2463	0.58	1.62	21.6	0.13	8.04
SD26-25	18.67	3.29	2323	2.52	2.15	NS	NS	0.63	1.61	22.4	0.15	3.86
SD26-26	19.22	2.93	2331	2.74	2.17	1655063	985	0.73	1.61	23.4	0.17	5.24
SD26-27	17.95	3.12	2340	2.84	2.04	2898002	3582	0.7	1.73	27.6	0.19	5.39

Parameter	Complex. Capacity	D. excen-tricus EC50	M. gallopro-vincialis EC50	S. purpur-atus EC50	L_{tot}	K_L
Data Units	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	
Data Type	Lab	Lab	Lab	Lab	Lab	Lab
Data Source	SPAWAR	SPAWAR	SPAWAR	SPAWA R	SPAWAR	SPAWAR
Comments	by ISE	Toxicity	Toxicity	Toxicity	by DPASV	by DPASV
Sample ID						
SD26-01	9.94	19.71	NS	NS	NS	NS
SD26-02	NS	NS	NS	NS	NS	NS
SD26-03	NS	NS	NS	NS	NS	NS
SD26-04	NS	NS	NS	NS	NS	NS
SD26-05	7.97	9.81	NS	NS	NS	NS
SD26-06	NS	9.30	NS	NS	NS	NS
SD26-07	NS	NS	NS	NS	NS	NS
SD26-08	NS	NS	NS	NS	NS	NS
SD26-09	NS	NS	NS	NS	NS	NS
SD26-10	NS	NS	NS	NS	NS	NS
SD26-11	NS	NS	NS	NS	NS	NS
SD26-12	NS	NS	NS	NS	NS	NS
SD26-13	9.62	13.44	NS	NS	NS	NS
SD26-14	NS	NS	NS	NS	NS	NS
SD26-15	NS	NS	NS	NS	NS	NS
SD26-16	NS	NS	NS	NS	NS	NS
SD26-17	NS	NS	NS	NS	NS	NS
SD26-18	7.85	NS	NS	NS	NS	NS
SD26-19	NS	NS	NS	NS	NS	NS
SD26-20	NS	NS	NS	NS	NS	NS
SD26-21	NS	NS	NS	NS	NS	NS
SD26-22	9.92	NS	NS	NS	NS	NS
SD26-23	NS	NS	NS	NS	NS	NS
SD26-24	NS	NS	NS	NS	NS	NS
SD26-25	NS	NS	NS	NS	NS	NS
SD26-26	22.57	31.22	NS	NS	NS	NS
SD26-27	NS	27.30	NS	NS	NS	NS

SD27: January 2001

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Parameter	Time	Residence Time	In Situ Temp	In Situ pH	In Situ Light Trans. @ 670 nm	In Situ UVF	In Situ Salinity	Density	In Situ Oxygen	In Situ Oxygen
Data Units	Day of Jan 2001	(days)	(°C)	(NBS)	(%)	(ug/L DFM)	(psu)	(sigma-t)	(mg/L)	(% sat.)
Data Type		model	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ
Data Source	SPAWAR	SD1D	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments										
Sample ID										
SD26-01	30.33530	0.00	13.621	8.152	81.90	174.83	33.47	25.09	5.62	95.09
SD26-02	30.34760	0.05	13.596	8.149	82.18	185.63	33.47	25.08	5.63	95.36
SD26-03	30.35880	0.15	13.628	8.149	83.07	212.67	33.44	25.06	5.66	95.82
SD26-04	30.36800	0.36	13.656	8.144	83.68	215.77	33.43	25.05	5.67	96.07
SD26-05	30.37710	0.74	13.663	8.136	83.49	254.41	33.40	25.02	5.68	96.25
SD26-06	30.39150	NS	13.692	8.127	74.28	472.46	33.17	24.84	5.68	96.09
SD26-07	30.40240	1.18	13.675	8.125	82.67	339.70	33.32	24.96	5.68	96.27
SD26-08	30.41500	1.63	13.699	8.127	82.35	342.96	33.31	24.95	5.72	96.94
SD26-09	30.42480	NS	13.655	8.093	76.82	557.52	33.11	24.80	5.51	93.16
SD26-10	30.43230	2.30	13.683	8.118	81.83	416.98	33.24	24.89	5.71	96.71
SD26-11	30.44530	3.19	13.658	8.114	80.99	517.73	33.13	24.81	5.75	97.25
SD26-12	30.45560	4.17	13.677	8.115	80.38	533.86	33.11	24.80	5.77	97.53
SD26-13	30.46670	5.79	13.653	8.114	80.25	590.12	33.04	24.75	5.79	97.89
SD26-14	30.47920	7.47	13.657	8.105	79.08	610.69	33.01	24.72	5.74	97.00
SD26-15	30.49010	8.44	13.727	8.106	77.53	608.85	33.00	24.70	5.74	97.16
SD26-16	30.49800	9.33	13.710	8.105	77.98	617.93	32.98	24.68	5.75	97.24
SD26-17	30.50620	10.71	13.681	8.101	80.70	636.97	32.94	24.66	5.72	96.72
SD26-18	30.52190	12.60	13.473	8.121	81.25	713.62	32.80	24.59	5.88	98.79
SD26-19	30.54150	14.99	13.602	8.124	80.84	698.12	32.80	24.57	5.89	99.27
SD26-20	30.55970	17.83	13.719	8.124	81.58	701.94	32.78	24.53	5.93	100.25
SD26-21	30.58030	20.49	13.756	8.134	80.65	725.23	32.72	24.47	6.01	101.49
SD26-22	30.59930	22.79	13.799	8.137	78.87	732.60	32.69	24.44	6.04	102.18
SD26-23	30.61670	25.19	13.870	8.143	76.69	746.35	32.62	24.38	6.10	103.22
SD26-24	30.63250	27.63	13.815	8.173	73.47	762.91	32.57	24.35	6.28	106.24
SD26-25	30.65090	30.06	13.923	8.187	73.36	762.66	32.58	24.34	6.40	108.43
SD26-26	30.66020	33.57	14.135	8.207	63.89	762.25	32.55	24.27	6.54	111.21
SD26-27	30.68570	37.64	14.328	8.216	44.53	803.21	32.27	24.01	6.39	108.81

Parameter	Flow Thru UVF	Flow Thru Chl-a	Flow Thru Cu Jalpaite ISE	Flow Thru Cu Chalcog. ISE	Flow Thru pH	pH2 TMA Cu	pH8 TMA Cu	total Cu	diss. Cu	total Zn	diss. Zn	TSS
Data Units	(volts)	(ug/L)	(pCu)	(pCu)	(NBS)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(mg/L)
Data Type	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Lab	Lab	Lab	Lab	Lab
Data Source	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments												
Sample ID												
SD26-01	4.562	0.030	11.46	10.56	8.085	0.3	NS	0.5	0.4	2.13	1.80	1.10
SD26-02	4.429	0.028	11.32	10.77	8.082	0.3	NS	0.5	0.5	1.94	1.85	0.76
SD26-03	4.489	0.029	11.63	10.96	8.085	0.1	NS	0.6	0.6	2.96	2.42	0.60
SD26-04	4.399	0.028	12.30	11.22	8.083	0.4	NS	0.7	0.7	2.8	2.78	0.86
SD26-05	4.706	0.029	12.93	11.67	8.076	0.3	NS	0.8	0.7	3.3	2.60	0.80
SD26-06	4.084	0.037	11.06	11.04	8.063	4.6	NS	5.6	4.5	24.3	19.9	0.90
SD26-07	4.035	0.031	11.58	11.14	8.065	1.4	NS	1.7	1.4	7.4	5.42	0.51
SD26-08	4.161	0.032	11.85	11.20	8.066	0.9	NS	1.4	1.2	6.1	4.6	0.84
SD26-09	4.375	0.031	11.55	11.16	8.035	2.7	NS	4.1	3.5	19.1	15.9	1.02
SD26-10	4.408	0.034	11.82	11.21	8.056	1.5	NS	1.9	1.8	9.9	8.9	0.80
SD26-11	4.278	0.035	11.90	11.24	8.050	1.4	NS	2.4	2.0	12.0	10.5	0.98
SD26-12	4.117	0.036	11.93	11.25	8.049	1.6	NS	2.4	1.9	12.5	7.7	0.61
SD26-13	3.573	0.036	11.93	11.23	8.056	1.5	NS	2.6	2.4	12.5	10.0	0.14
SD26-14	3.908	0.035	11.94	11.21	8.054	1.5	NS	2.7	2.5	13.4	10.2	0.32
SD26-15	4.457	0.033	11.96	11.21	8.054	1.7	NS	2.5	2.5	12.8	10.3	0.36
SD26-16	4.421	0.034	11.97	11.19	8.053	1.3	NS	2.6	2.5	12.7	10.2	0.90
SD26-17	4.573	0.032	11.96	11.15	8.050	1.6	NS	2.8	2.5	13.1	10.2	0.92
SD26-18	4.792	0.033	12.00	11.17	8.060	1.9	NS	3.0	3.1	14.8	11.4	1.03
SD26-19	4.924	0.033	11.99	11.15	8.050	2.0	NS	3.2	2.7	14.1	13.0	0.52
SD26-20	4.925	0.035	11.92	11.06	8.052	2.0	NS	3.4	2.8	15.0	13.3	0.20
SD26-21	4.883	0.036	11.97	11.00	8.057	1.9	NS	3.5	3.0	14.2	12.9	0.82
SD26-22	4.977	0.038	11.93	10.94	8.056	1.8	NS	3.5	3.2	13.9	11.6	0.88
SD26-23	4.861	0.040	12.02	10.89	8.055	1.77	NS	3.5	3.1	14.2	11.3	0.92
SD26-24	4.740	0.040	12.11	10.87	8.096	1.7	NS	3.2	3.1	12.3	9.7	1.53
SD26-25	4.714	0.040	12.15	10.85	8.108	1.5	NS	3.3	3.0	12.0	9.1	1.48
SD26-26	4.704	0.041	12.20	10.84	8.128	1.1	NS	3.3	2.8	11.8	9.6	2.02
SD26-27	4.787	0.047	12.36	10.85	8.139	1.0	NS	2.5	2.3	7.1	6.6	4.46

Parameter	Bacterial Production	DOC	Total Alkalinity	Chloro-phyll	Phaeo-pigments	Bact. Abund.	Cyano Abund.	NO_3	PO_4	Si	NO_2	NH_3
Data Units	(ugC/L/d)	(mg/L)	um kg^{-1}	(mg m^{-3})	(mg m^{-3})	(ml^{-1})	(ml^{-1})	(uM)	(uM)	(uM)	(uM)	(uM)
Data Type	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
Data Source	NRL Boyd	NRL Boyd	UABC Ayon	SIO Holm-Hansen	SIO Holm-Hansen	SIO Holm-Hansen	SIO Holm-Hansen	SIO ODF	SIO ODF	SIO ODF	SIO ODF	SIO ODF
Comments												
Sample ID												
SD26-01	2.18	1.36	2375	1.10	0.44	1443056	11625	1.02	0.59	3	0.12	0.66
SD26-02	4.35	1.84	2443	0.97	0.54	1375598	11625	0.95	0.59	2.9	0.13	0.66
SD26-03	4.12	1.20	2386	1.01	0.47	1488275	11075	1.14	0.6	3.2	0.14	0.7
SD26-04	4.22	1.19	NS	1.04	0.48	2093914	9390	1.17	0.62	3.3	0.14	0.86
SD26-05	3.66	1.26	2386	1.08	0.43	2460115	8764	1.19	0.63	3.2	0.14	0.85
SD26-06	6.11	1.39	2410	1.81	0.77	1441327	2340	1.29	0.69	4.1	0.12	0.71
SD26-07	4.83	1.31	2419	1.85	0.51	1572783.13	5868.59	1.38	0.71	4.1	0.15	0.94
SD26-08	3.87	1.26	2353	1.69	0.54	1568088	5962	1.3	0.68	3.9	0.14	0.87
SD26-09	6.88	1.39	2394	1.63	0.51	2117389	2313	1.92	0.81	5.4	0.18	1.06
SD26-10	3.86	1.37	NS	1.98	0.58	1699545	3162	1.77	0.74	4.4	0.16	0.86
SD26-11	3.77	1.46	NS	2.51	0.71	2056355	2116	1.63	0.81	4.7	0.16	0.82
SD26-12	4.12	1.42	NS	2.56	0.77	1863865	1334	1.68	0.8	4.8	0.16	0.92
SD26-13	4.70	1.51	2347	2.69	0.79	2248845.13	1329.52	1.78	0.85	5	0.17	0.85
SD26-14	3.55	1.53	2361	2.67	0.77	2023491	518	1.95	0.9	5.1	0.18	1.08
SD26-15	4.03	1.52	NS	2.35	0.63	2117389	2038	2.01	0.91	5.2	0.18	1.04
SD26-16	4.54	1.78	2333	2.43	0.60	2070440	455	2.01	0.9	5.2	0.18	1.05
SD26-17	5.20	1.64	2358	2.35	0.59	2107999	220	2.09	0.96	5.4	0.18	1.15
SD26-18	7.33	1.67	2423	1.83	0.53	2427250	96	1.92	0.99	5.7	0.17	0.99
SD26-19	5.70	1.65	2358	1.83	0.59	2394386.25	288.92	1.81	0.97	5.7	0.17	0.93
SD26-20	7.09	1.70	NS	1.98	0.59	2239455	482	1.81	1.01	5.6	0.17	0.89
SD26-21	7.41	1.73	2404	2.14	0.81	2399081.13	288.92	1.79	0.99	5.5	0.17	0.74
SD26-22	8.40	1.68	2431	2.28	0.67	2427250	289	1.23	0.76	3.8	0.12	0.45
SD26-23	7.77	1.72	2574	2.75	0.92	2450725	1059	1.2	0.8	4.3	0.12	0.44
SD26-24	10.27	1.84	NS	2.07	0.80	2446030	578	1.25	0.99	5.4	0.13	0.57
SD26-25	10.53	1.94	2530	2.37	0.96	2605655.63	481.53	1.26	0.94	5.5	0.14	0.42
SD26-26	10.50	2.20	2374	2.37	0.96	2492979	867	1.26	0.92	6	0.15	0.56
SD26-27	11.85	1.95	2398	2.43	1.28	3070448	482	1.07	0.95	7.9	0.17	0.67

Parameter	Complex. Capacity	D. excen-tricus EC50	M. gallopro-vincialis EC50	S. purpur-atus EC50	L_{tot}	K_L
Data Units	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	
Data Type	Lab	Lab	Lab	Lab	Lab	Lab
Data Source	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments	by ISE	Toxicity	Toxicity	Toxicity	by DPASV	by DPASV
Sample ID						
SD26-01	7.94	NS	NS	NS	3.93	1.24E+08
SD26-02	6.22	NS	NS	NS	NS	NS
SD26-03	7.65	NS	NS	NS	5.07	4.29E+07
SD26-04	9.15	NS	3.59	NS	4.26	4.61E+07
SD26-05	NS	NS	NS	NS	NS	NS
SD26-06	NS	NS	<5.6	NS	NS	NS
SD26-07	8.18	NS	NS	NS	NS	NS
SD26-08	NS	NS	NS	NS	NS	NS
SD26-09	NS	NS	NS	NS	NS	NS
SD26-10	NS	NS	NS	NS	NS	NS
SD26-11	NS	NS	NS	NS	NS	NS
SD26-12	NS	NS	NS	NS	NS	NS
SD26-13	NS	NS	NS	NS	NS	NS
SD26-14	10.84	NS	NS	NS	NS	NS
SD26-15	11.22	NS	NS	NS	6.35	1.01E+08
SD26-16	NS	NS	NS	NS	NS	NS
SD26-17	NS	NS	NS	NS	NS	NS
SD26-18	16.48	NS	NS	NS	6.33	4.16E+07
SD26-19	12.55	NS	NS	NS	4.68	3.13E+07
SD26-20	9.58	NS	NS	NS	NS	NS
SD26-21	NS	NS	NS	NS	NS	NS
SD26-22	NS	NS	NS	NS	NS	NS
SD26-23	10.90	NS	NS	NS	NS	NS
SD26-24	13.90	NS	NS	NS	5.44	4.92E+07
SD26-25	12.82	NS	4.92	NS	NS	NS
SD26-26	14.91	NS	<3.3	NS	NS	NS
SD26-27	NS	NS	12.95	NS	NS	NS

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Parameter	Time	Residence Time	In Situ Temp	In Situ pH	In Situ Light Trans. @ 670 nm	In Situ UVF	In Situ Salinity	Density	In Situ Oxygen	In Situ Oxygen
Data Units	Day of May 2001	(days)	(^{o}C)	(NBS)	(%)	(ug/L DFM)	(psu)	(sigma-t)	(mg/L)	(% sat.)
Data Type		model	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ
Data Source	SPAWAR	SD1D	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments										
Sample ID										
SD26-01	11.32835	0.00	17.482	8.272	65.58	243.58	33.67	24.38	6.91	126.52
SD26-02	11.33883	0.05	17.725	8.262	67.53	262.67	33.67	24.32	6.92	127.40
SD26-03	11.34913	0.15	18.064	8.246	62.13	299.09	33.68	24.25	6.75	125.10
SD26-04	11.35682	0.36	18.079	8.244	51.04	301.42	33.68	24.25	6.76	125.31
SD26-05	11.36453	0.74	18.427	8.231	57.54	330.37	33.69	24.17	6.63	123.59
SD26-06	11.37786	NS	19.149	8.223	64.87	383.38	33.72	24.00	6.60	124.75
SD26-07	11.40761	1.18	18.644	8.212	57.07	348.49	33.70	24.12	6.56	122.93
SD26-08	11.41636	1.63	18.818	8.208	55.10	364.10	33.71	24.08	6.52	122.51
SD26-09	11.42427	NS	19.158	8.187	47.85	433.92	33.72	24.00	6.29	118.95
SD26-10	11.43364	2.30	18.859	8.204	47.14	365.77	33.71	24.07	6.53	122.82
SD26-11	11.44604	3.19	19.080	8.197	47.71	382.92	33.71	24.02	6.44	121.62
SD26-12	11.45471	4.17	19.281	8.185	53.11	403.09	33.72	23.97	6.35	120.32
SD26-13	11.46448	5.79	19.394	8.175	54.02	406.83	33.73	23.95	6.25	118.82
SD26-14	11.47620	7.47	19.562	8.166	54.89	418.80	33.73	23.91	6.19	117.93
SD26-15	11.48499	8.44	19.587	8.164	59.04	423.37	33.73	23.91	6.17	117.71
SD26-16	11.49115	9.33	19.505	8.164	58.06	415.90	33.73	23.92	6.17	117.50
SD26-17	11.49749	10.71	19.582	8.159	57.13	420.75	33.73	23.90	6.11	116.58
SD26-18	11.51160	12.60	19.891	8.149	57.28	439.61	33.75	23.84	6.05	116.08
SD26-19	11.52912	14.99	20.119	8.140	56.32	451.54	33.77	23.79	5.95	114.62
SD26-20	11.54628	17.83	20.303	8.140	56.71	452.55	33.78	23.75	5.97	115.30
SD26-21	11.57993	20.49	20.596	8.138	55.33	468.01	33.81	23.70	5.93	115.27
SD26-22	11.59523	22.79	20.690	8.137	54.98	478.94	33.83	23.68	5.93	115.41
SD26-23	11.60955	25.19	20.974	8.138	50.69	492.76	33.87	23.64	5.86	114.76
SD26-24	11.62133	27.63	21.221	8.143	51.25	504.92	33.90	23.60	5.85	115.06
SD26-25	11.63168	30.06	21.490	8.152	46.37	507.88	33.94	23.56	5.89	116.47
SD26-26	11.64315	33.57	22.024	8.135	42.10	550.04	34.05	23.49	5.56	111.01
SD26-27	11.66039	37.64	22.268	8.139	28.65	526.64	34.12	23.47	5.59	112.19

Parameter	Flow Thru UVF	Flow Thru Chl-a	Flow Thru Cu Jalpaite ISE	Flow Thru Cu Chalcog. ISE	Flow Thru pH	pH2 TMA Cu	pH2 TMA Zn	total Cu	diss. Cu	total Zn	diss. Zn	TSS
Data Units	(volts)	(ug/L)	(pCu)	(pCu)	(NBS)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(mg/L)
Data Type	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Lab	Lab	Lab	Lab	Lab
Data Source	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments												
Sample ID												
SD26-01	0.460	0.035	13.21	12.62	8.173	-0.6	1.2	0.7	0.6	2.01	1.68	3.17
SD26-02	0.548	0.035	13.25	12.68	8.161	-0.2	1.3	0.7	0.6	1.97	1.55	2.58
SD26-03	0.713	0.038	13.25	12.66	8.147	-0.2	1.1	1.0	0.9	2.84	2.29	2.40
SD26-04	0.716	0.037	13.70	13.29	8.143	-0.1	1.1	1.1	0.9	2.9	2.44	3.12
SD26-05	0.901	0.038	13.96	13.52	8.132	-0.3	1.1	1.2	1.0	3.3	2.62	2.56
SD26-06	1.191	0.043	12.02	11.40	8.124	3.8	3.2	5.7	4.5	16.0	13.7	1.52
SD26-07	0.992	0.038	12.84	12.55	8.120	0.3	1.4	1.5	1.3	4.2	3.62	3.19
SD26-08	1.063	0.041	12.90	12.58	8.115	0.3	1.8	1.4	1.3	4.3	3.6	5.13
SD26-09	1.421	0.045	12.58	12.09	8.096	1.1	3.7	3.4	2.7	10.6	9.2	3.34
SD26-10	1.080	0.041	12.75	12.47	8.114	0.4	2.3	1.5	1.3	4.8	3.8	3.79
SD26-11	1.184	0.043	12.92	12.65	8.107	0.3	3.10	1.6	1.3	4.5	3.9	4.32
SD26-12	1.265	0.041	12.93	12.61	8.097	0.3	2.86	1.9	1.7	5.7	5.4	3.26
SD26-13	1.302	0.039	12.94	12.62	8.088	0.6	2.55	1.9	1.7	6.0	5.3	4.28
SD26-14	1.360	0.038	12.93	12.60	8.080	0.3	1.8	2.0	1.8	6.5	5.5	3.04
SD26-15	1.384	0.038	12.93	12.59	8.080	0.6	NS	2.0	1.8	6.6	5.4	2.63
SD26-16	1.346	0.037	12.93	12.59	8.081	0.5	2.4	1.9	1.8	6.5	5.5	3.02
SD26-17	1.375	0.036	12.92	12.58	8.077	0.3	NS	2.0	1.8	6.8	5.6	6.83
SD26-18	1.481	0.041	12.99	12.68	8.070	0.9	2.2	2.0	1.9	6.3	5.5	2.72
SD26-19	1.563	0.041	13.02	12.71	8.064	2.6	NS	2.5	2.1	7.7	6.1	2.51
SD26-20	1.553	0.041	12.92	12.59	8.066	NS	1.2	2.5	2.1	7.6	5.9	2.78
SD26-21	1.639	0.044	12.85	12.52	8.068	2.9	NS	2.5	2.2	7.5	6.5	2.91
SD26-22	1.690	0.048	12.87	12.53	8.069	2.7	NS	2.6	2.3	7.6	6.3	2.85
SD26-23	1.795	0.052	12.88	12.54	8.070	2.22	6.1	2.8	2.3	7.0	6.5	3.11
SD26-24	1.879	0.053	12.95	12.59	8.074	2.1	1.9	2.8	2.2	6.7	5.3	3.79
SD26-25	1.937	0.055	12.99	12.65	8.083	NS	1.0	2.7	2.3	6.1	5.6	5.28
SD26-26	2.206	0.063	13.05	12.70	8.070	2.4	0.4	2.7	2.3	6.3	6.1	3.76
SD26-27	2.223	0.073	13.11	12.79	8.075	2.5	0.4	2.7	2.2	6.0	4.9	7.48

Parameter	Bacterial Production	DOC	Total Alkalinity	Chloro-phyll	Phaeo-pigments	Bact. Abund.	Cyano Abund.	NO_3	PO_4	Si	NO_2	NH_3
Data Units	(ugC/L/d)	(mg/L)	um kg^{-1}	(mg m^{-3})	(mg m^{-3})	(ml^{-1})	(ml^{-1})	(uM)	(uM)	(uM)	(uM)	(uM)
Data Type	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
Data Source	NRL Boyd	NRL Boyd	UABC Ayon	SIO Holm-Hansen	SIO Holm-Hansen	SIO Holm-Hansen	SIO Holm-Hansen	SIO ODF	SIO ODF	SIO ODF	SIO ODF	SIO ODF
Comments												
Sample ID												
SD26-01	17.57	1.50	NS	1.04	1.35	NS	54774	0.69	0.53	6	0.05	1.05
SD26-02	14.65	1.59	NS	1.24	1.08	NS	33177	0.44	0.57	6.7	0.04	1.36
SD26-03	13.34	1.76	NS	1.87	1.14	NS	10915	0.18	0.6	8.1	0.04	1.29
SD26-04	15.33	1.64	NS	1.70	1.26	NS	31299	0.79	0.65	8.2	0.04	1.62
SD26-05	13.95	1.56	NS	1.90	1.28	NS	15890	0.18	0.65	9.1	0.04	1.39
SD26-06	13.70	1.65	NS	2.04	1.11	NS	3099	0.16	0.71	10	0.04	1.17
SD26-07	12.73	1.64	NS	1.90	1.32	NS	14954.05	0.18	0.74	9.9	0.05	1.71
SD26-08	11.65	1.48	NS	1.92	1.26	NS	8488	0.15	0.71	10.4	0.04	1.49
SD26-09	10.94	1.65	NS	2.35	1.52	NS	5759	0.26	0.78	11.3	0.06	1.47
SD26-10	12.43	1.75	NS	2.06	1.34	NS	9452	0.19	0.73	10.8	0.05	1.51
SD26-11	9.26	1.69	NS	2.67	1.48	NS	3288	0.29	0.75	11	0.05	1.47
SD26-12	5.55	1.74	NS	2.24	1.17	NS	4820	0.15	0.78	11.7	0.05	1.42
SD26-13	10.27	1.70	NS	2.14	1.17	NS	2816.93	0.24	0.83	12.2	0.05	1.53
SD26-14	10.56	1.76	NS	2.06	1.17	NS	3193	0.33	0.87	12.5	0.05	1.58
SD26-15	9.50	1.65	NS	1.90	1.04	NS	2128	0.24	0.87	12.9	0.05	1.59
SD26-16	9.53	1.65	NS	1.76	1.08	NS	3443	0.28	0.83	12.5	0.05	1.57
SD26-17	10.60	1.63	NS	1.79	1.14	NS	3099	0.55	0.9	12.7	0.05	1.74
SD26-18	13.81	1.66	NS	1.68	1.28	NS	1941	0.2	0.93	13.2	0.05	1.4
SD26-19	6.33	1.79	NS	1.61	1.24	NS	1502.36	0.26	0.96	13.6	0.06	1.36
SD26-20	10.03	1.81	NS	1.64	1.15	NS	1440	0.26	0.93	14.2	0.05	1.27
SD26-21	9.43	1.86	NS	1.96	1.54	NS	876.38	0.11	0.96	15.4	0.04	0.76
SD26-22	10.16	1.74	NS	2.05	1.21	NS	751	0.08	0.94	15.7	0.04	0.63
SD26-23	9.16	1.81	NS	2.88	1.64	NS	626	0.21	0.98	16.4	0.05	0.73
SD26-24	12.58	1.84	NS	2.76	1.97	NS	626	0.08	0.98	15.3	0.04	0.54
SD26-25	14.97	1.88	NS	2.88	1.89	NS	438.19	0.06	0.94	15.7	0.04	0.45
SD26-26	17.29	1.93	NS	4.35	2.15	NS	563	0.69	0.99	20.1	0.08	1.17
SD26-27	16.02	2.00	NS	4.76	2.36	NS	188	0.18	0.97	20.2	0.08	0.62

Parameter	Complex. Capacity	D. excen-tricus EC50	M. gallopro-vincialis EC50	S. purpur-atus EC50	L_{tot}	K_L
Data Units	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	
Data Type	Lab	Lab	Lab	Lab	Lab	Lab
Data Source	SPAWAR	SPAWAR	SPAWAR	SPAWA R	SPAWAR	SPAWAR
Comments	by ISE	Toxicity	Toxicity	Toxicity	by DPASV	by DPASV
Sample ID						
SD26-01	10.94	NS	NS	NS	9.48	6.93E+07
SD26-02	NS	NS	3.15	NS	11.43	1.30E+08
SD26-03	NS	NS	NS	NS	NS	NS
SD26-04	NS	NS	NS	NS	4.82	4.54E+07
SD26-05	12.43	NS	NS	NS	9.67	3.22E+07
SD26-06	NS	NS	NS	NS	NS	NS
SD26-07	14.63	NS	NS	NS	9.45	3.91E+07
SD26-08	NS	NS	6.04	NS	10.23	5.89E+07
SD26-09	NS	NS	NS	NS	NS	NS
SD26-10	NS	NS	6.25	NS	9.34	7.73E+07
SD26-11	12.27	NS	NS	NS	12.24	4.54E+07
SD26-12	NS	NS	NS	NS	NS	NS
SD26-13	NS	NS	NS	NS	NS	NS
SD26-14	10.41	NS	NS	NS	9.13	2.41E+07
SD26-15	NS	NS	6.74	NS	9.92	9.29E+07
SD26-16	NS	NS	NS	NS	NS	NS
SD26-17	14.03	NS	NS	NS	8.25	5.88E+07
SD26-18	NS	NS	NS	NS	NS	NS
SD26-19	NS	NS	NS	NS	NS	NS
SD26-20	11.12	NS	NS	NS	7.55	5.68E+07
SD26-21	NS	NS	NS	NS	NS	NS
SD26-22	NS	NS	7.54	NS	10.08	4.34E+07
SD26-23	12.16	NS	NS	NS	10.81	5.59E+07
SD26-24	11.35	NS	NS	NS	11.11	1.28E+07
SD26-25	13.58	NS	7.34	NS	8.94	8.73E+07
SD26-26	13.36	NS	NS	NS	9.29	2.93E+07
SD26-27	16.15	NS	NS	NS	8.89	6.29E+07

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Parameter	Time	Residence Time	In Situ Temp	In Situ pH	In Situ Light Trans. @ 670 nm	In Situ UVF	In Situ Salinity	Density	In Situ Oxygen	In Situ Oxygen
Data Units	Day of Sept 2001	(days)	(^{o}C)	(NBS)	(%)	(ug/L DFM)	(psu)	(sigma-t)	(mg/L)	(% sat.)
Data Type		model	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ
Data Source	SPAWAR	SD1D	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments										
Sample ID										
SD26-01	19.35675	0.00	16.618	8.211	70.69	204.96	33.52	24.47	6.77	121.86
SD26-02	19.36574	0.05	16.335	8.222	64.45	217.38	33.50	24.51	6.89	123.23
SD26-03	19.37628	0.15	16.538	8.216	57.37	222.91	33.45	24.44	6.73	120.83
SD26-04	19.38730	0.36	16.555	8.213	63.15	223.32	33.48	24.45	6.75	121.16
SD26-05	19.40230	0.74	16.940	8.182	61.11	239.23	33.52	24.39	6.49	117.54
SD26-06	19.42516	NS	18.045	8.143	62.18	302.54	33.62	24.20	6.09	112.60
SD26-07	19.45100	1.18	16.286	8.226	61.14	240.08	33.46	24.50	7.01	125.23
SD26-08	19.46592	1.63	17.029	8.222	61.35	233.06	33.50	24.35	6.72	121.76
SD26-09	19.47762	NS	19.167	8.140	59.19	349.54	33.75	24.02	5.80	109.73
SD26-10	19.48896	2.30	17.562	8.192	59.28	261.67	33.57	24.28	6.50	119.03
SD26-11	19.50444	3.19	17.978	8.169	57.18	277.37	33.62	24.22	6.20	114.62
SD26-12	19.51915	4.17	19.733	8.131	57.46	340.37	33.83	23.94	5.62	107.35
SD26-13	19.52607	5.79	20.052	8.123	57.79	354.30	33.88	23.89	5.57	107.11
SD26-14	19.54084	7.47	20.240	8.105	56.18	364.14	33.91	23.87	5.54	107.10
SD26-15	19.55140	8.44	20.497	8.091	55.39	371.11	33.95	23.83	5.29	102.80
SD26-16	19.55875	9.33	20.561	8.086	60.70	378.34	33.96	23.82	5.28	102.60
SD26-17	19.56649	10.71	20.913	8.087	62.48	379.97	34.00	23.76	5.25	102.72
SD26-18	19.58333	12.60	21.496	8.087	63.86	399.84	34.10	23.67	5.22	103.29
SD26-19	19.60289	14.99	21.535	8.079	61.23	387.90	34.11	23.67	5.20	103.03
SD26-20	19.61912	17.83	22.057	8.082	61.46	404.58	34.23	23.62	5.12	102.38
SD26-21	19.63722	20.49	22.489	8.083	57.49	411.26	34.35	23.59	5.04	101.64
SD26-22	19.65412	22.79	22.791	8.079	57.19	423.28	34.47	23.59	4.92	99.84
SD26-23	19.67362	25.19	23.564	8.089	49.79	451.66	34.80	23.62	4.73	97.52
SD26-24	19.69063	27.63	23.807	8.088	44.40	460.75	34.97	23.67	4.64	96.24
SD26-25	19.70296	30.06	24.079	8.088	35.51	469.98	35.15	23.74	4.59	96.03
SD26-26	19.72086	33.57	24.272	8.098	31.24	482.87	35.31	23.80	4.56	95.35
SD26-27	19.74305	37.64	24.218	8.128	33.32	492.48	35.50	23.96	4.60	96.40

Parameter	Flow Thru UVF	Flow Thru Chl-a	Flow Thru Cu Jalpaite ISE	Flow Thru Cu Chalcog. ISE	Flow Thru pH	pH2 TMA Cu	pH2 TMA Zn	total Cu	diss. Cu	total Zn	diss. Zn	TSS
Data Units	(volts)	(ug/L)	(pCu)	(pCu)	(NBS)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(mg/L)
Data Type	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Lab	Lab	Lab	Lab	Lab
Data Source	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments												
Sample ID												
SD26-01	0.867	0.046	12.71	12.65	8.046	-0.4	0.0	0.3	0.3	0.97	0.64	1.93
SD26-02	0.954	0.050	12.74	12.70	8.069	-0.6	0.0	0.3	0.2	0.78	0.38	NS
SD26-03	0.987	0.052	12.77	12.75	8.056	NS	-0.1	0.3	0.2	1.07	0.38	5.72
SD26-04	0.970	0.047	12.82	12.82	8.057	0.9	0.4	0.3	0.2	0.8	0.33	3.11
SD26-05	1.051	0.046	12.79	12.80	8.056	1.6	1.0	0.5	0.3	1.4	0.83	3.10
SD26-06	1.469	0.047	12.36	12.40	7.967	2.5	3.5	2.8	2.1	7.5	6.7	1.76
SD26-07	1.091	0.052	12.66	12.81	8.065	0.5	0.4	0.4	0.3	1.1	0.61	4.39
SD26-08	0.986	0.042	12.74	12.93	8.061	0.4	0.5	0.5	0.4	1.4	0.8	3.88
SD26-09	1.703	0.042	12.37	12.54	7.980	4.0	2.1	2.9	2.3	8.7	7.4	5.00
SD26-10	1.167	0.045	12.62	12.84	8.040	0.9	2.2	1.0	0.7	2.9	2.1	2.95
SD26-11	1.266	0.045	12.70	12.92	8.022	0.6	1.71	1.0	0.7	2.7	2.0	2.91
SD26-12	1.675	0.041	12.67	12.89	7.974	0.9	2.85	2.0	1.5	6.2	4.8	2.50
SD26-13	1.777	0.042	12.66	12.87	7.968	0.9	3.22	2.0	1.7	6.8	5.9	2.60
SD26-14	1.858	0.041	12.64	12.88	7.960	0.8	4.2	2.1	1.7	7.3	5.9	3.42
SD26-15	1.919	0.036	12.65	12.91	7.946	0.7	3.3	2.3	1.8	7.5	5.8	4.41
SD26-16	1.963	0.035	12.63	12.89	7.946	4.1	4.0	2.3	1.8	7.7	6.2	2.16
SD26-17	1.980	0.034	12.61	12.88	7.948	2.9	4.3	2.3	1.8	8.0	6.7	2.16
SD26-18	2.095	0.038	12.59	12.89	7.950	2.1	4.1	2.5	2.2	8.7	7.3	1.75
SD26-19	2.007	0.037	12.54	12.85	7.946	1.9	4.1	2.7	2.2	8.1	6.6	2.55
SD26-20	2.124	0.039	12.53	12.85	7.945	1.8	3.5	2.9	2.3	8.6	6.9	1.93
SD26-21	2.192	0.039	12.54	12.88	7.947	1.6	4.2	3.1	2.6	8.7	7.4	2.68
SD26-22	2.281	0.038	12.55	12.90	7.944	1.6	4.8	3.0	2.7	8.6	6.9	3.30
SD26-23	2.549	0.041	12.67	13.04	7.955	1.32	5.2	3.3	2.7	8.1	6.8	3.91
SD26-24	2.657	0.041	12.76	13.12	7.954	1.6	4.8	2.7	2.6	7.7	6.5	5.00
SD26-25	2.742	0.047	12.76	13.14	7.952	1.3	4.7	3.5	2.4	7.8	4.7	9.12
SD26-26	3.004	0.049	12.78	13.19	7.967	1.7	4.1	3.5	2.7	7.1	5.8	6.19
SD26-27	3.117	0.050	12.87	13.30	7.988	1.0	3.5	2.7	2.2	5.0	3.8	6.56

Parameter	Bacterial Production	DOC	Total Alkalinity	Chloro-phyll	Phaeo-pigments	Bact. Abund.	Cyano Abund.	NO_3	PO_4	Si	NO_2	NH_3
Data Units	(ugC/L/d)	(mg/L)	um kg^{-1}	(mg m^{-3})	(mg m^{-3})	(ml^{-1})	(ml^{-1})	(uM)	(uM)	(uM)	(uM)	(uM)
Data Type	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
Data Source	NRL Boyd	NRL Boyd	UABC Ayon	SIO Holm-Hansen	SIO Holm-Hansen	SIO Holm-Hansen	SIO Holm-Hansen	SIO ODF	SIO ODF	SIO ODF	SIO ODF	SIO ODF
Comments												
Sample ID												
SD26-01	16.40	2.99	2224	3.76	1.26	2260000	59300	0.07	0.42	4.5	0.03	0.35
SD26-02	24.47	2.55	2231	4.73	1.81	1740000	102000	0.07	0.43	4.3	0.03	0.52
SD26-03	32.98	2.66	2210	5.20	2.49	2280000	106000	0.15	0.49	5.2	0.06	0.75
SD26-04	31.47	2.85	2183.00	5.67	1.86	2480000	88200	0.25	0.45	5.2	0.04	0.97
SD26-05	28.28	2.49	2210	5.17	1.99	1960000	105000	0.1	0.5	6	0.04	0.43
SD26-06	35.02	1.55	2251	3.96	1.38	2270000	26300	0.22	0.63	8.2	0.05	0.93
SD26-07	34.85	2.39	2238	5.37	1.86	2360000.00	114000.00	0.12	0.43	4.9	0.03	0.34
SD26-08	30.78	2.64	2197	4.58	1.42	2370000	100000	0.08	0.47	5.6	0.02	0.42
SD26-09	24.31	2.31	2231	3.70	1.36	1940000	10800	0.3	0.75	10.8	0.06	0.78
SD26-10	20.05	2.62	2319	4.46	1.46	2840000	66000	0.13	0.61	7.9	0.04	0.52
SD26-11	23.87	1.96	2244	4.41	1.47	1980000	10800	0.14	0.47	5.5	0.06	0.47
SD26-12	29.20	3.16	2258	3.58	1.06	2190000	20500	0.42	0.81	11.5	0.08	1.09
SD26-13	26.83	2.68	2251	3.73	1.45	3020000.00	10200.00	1.15	0.81	11.1	0.08	1.02
SD26-14	25.63	2.44	2224	3.82	1.16	2240000	8310	0.52	0.87	12.2	0.09	1.14
SD26-15	30.34	2.29	2244	3.08	1.32	3450000	616	0.54	0.88	12.3	0.1	1.61
SD26-16	26.38	2.70	2224	2.94	1.26	2740000	4370	0.51	0.88	11.5	0.09	1.38
SD26-17	15.36	2.63	2231	2.63	1.20	2510000	4000	0.5	0.84	11.1	0.08	1.2
SD26-18	31.16	2.95	2366	2.42	1.34	2820000	2160	0.47	0.93	12.5	0.09	1.09
SD26-19	28.51	3.04	2312	2.29	1.33	1360000.00	328.00	0.51	0.95	13.2	0.12	1.15
SD26-20	29.45	3.39	2376.00	2.33	1.52	2530000	82	0.42	0.96	14	0.11	0.96
SD26-21	30.55	3.80	2339	2.30	1.63	1900000.00	410.00	0.51	0.99	14.7	0.11	1.01
SD26-22	32.57	2.92	2393	2.16	1.51	2100000	205	0.47	1.06	15.7	0.11	1.06
SD26-23	36.18	3.35	2272	2.58	1.57	2010000	0	0.36	1.15	19.5	0.12	1.25
SD26-24	39.79	3.59	2536	2.79	1.65	1620000	0	0.29	1.14	20.5	0.11	1.3
SD26-25	36.13	3.39	2427	3.20	2.14	2440000.00	308.00	0.23	1.18	21.5	0.12	1.04
SD26-26	35.36	3.38	2326	3.14	1.67	1340000	0	0.41	1.17	20.9	0.12	1.36
SD26-27	37.27	3.79	2448	3.52	1.78	2190000	82	0.15	1.19	24.8	0.09	0.68

Parameter	Complex. Capacity	D. excen-tricus EC50	M. gallopro-vincialis EC50	S. purpur-atus EC50	L_{tot}	K_L
Data Units	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	
Data Type	Lab	Lab	Lab	Lab	Lab	Lab
Data Source	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments	by ISE	Toxicity	Toxicity	Toxicity	by DPASV	by DPASV
Sample ID						
SD26-01	13.71	19.22	NS	NS	9.60	1.11E+08
SD26-02	NS	NS	NS	NS	11.41	4.52E+07
SD26-03	10.26	23.30	NS	NS	10.89	3.80E+07
SD26-04	9.82	23.04	NS	NS	7.32	6.49E+07
SD26-05	11.74	26.17	NS	NS	9.42	6.82E+07
SD26-06	NS	NS	NS	NS	NS	NS
SD26-07	16.99	27.70	NS	NS	6.41	1.76E+07
SD26-08	13.20	NS	NS	NS	6.38	7.35E+07
SD26-09	NS	22.21	NS	NS	NS	NS
SD26-10	NS	NS	NS	NS	NS	NS
SD26-11	12.42	27.21	NS	NS	10.47	4.62E+07
SD26-12	13.24	27.86	NS	NS	11.63	2.96E+07
SD26-13	16.48	20.60	NS	NS	12.55	4.37E+07
SD26-14	10.62	NS	NS	NS	10.05	4.21E+07
SD26-15	12.19	22.31	NS	NS	11.48	3.91E+07
SD26-16	12.58	29.86	NS	NS	13.74	3.53E+07
SD26-17	9.03	NS	NS	NS	1.45	8.75E+10
SD26-18	NS	NS	NS	NS	NS	NS
SD26-19	NS	NS	NS	NS	NS	NS
SD26-20	8.03	NS	NS	NS	8.53	6.40E+07
SD26-21	17.60	28.91	NS	NS	14.70	2.92E+07
SD26-22	NS	NS	NS	NS		
SD26-23	12.34	35.80	NS	NS	11.50	3.46E+07
SD26-24	NS	NS	NS	NS	NS	NS
SD26-25	18.17	34.26	NS	NS	9.57	7.88E+07
SD26-26	15.98	37.97	16.11	NS	10.88	5.62E+07
SD26-27	14.31	34.63	NS	NS	9.59	6.47E+07

SD33: January 2002

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Parameter	Time	Residence Time	In Situ Temp	In Situ pH	In Situ Light Trans. @ 670 nm	In Situ UVF	In Situ Salinity	Density	In Situ Oxygen	In Situ Oxygen
Data Units	Day of Jan 2002	(days)	(°C)	(NBS)	(%)	(ug/L DFM)	(psu)	(sigma-t)	(mg/L)	(% sat.)
Data Type		model	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ
Data Source	SPAWAR	SD1D	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments										
Sample ID										
SD26-01	27.36160	0.00	14.334	8.554	88.24	121.37	33.57	25.01	6.30	108.39
SD26-02	27.37600	0.05	14.443	8.544	78.65	148.90	33.60	25.01	6.21	107.03
SD26-03	27.39130	0.15	14.354	8.538	78.90	156.61	33.59	25.03	6.16	105.99
SD26-04	27.40040	0.36	14.387	8.523	75.75	169.73	33.61	25.03	6.02	103.68
SD26-05	27.40940	0.74	14.456	8.534	74.04	165.72	33.60	25.01	6.11	105.25
SD26-06	27.42420	NS	15.562	8.496	67.89	301.16	33.68	24.83	5.76	101.53
SD26-07	27.45250	1.18	14.552	8.540	73.47	160.28	33.60	24.99	6.22	107.40
SD26-08	27.47540	1.63	14.858	8.525	67.45	201.05	33.64	24.95	6.10	105.99
SD26-09	27.48460	NS	15.645	8.463	55.63	363.44	33.74	24.86	5.56	98.20
SD26-10	27.49590	2.30	15.192	8.498	63.07	264.87	33.70	24.93	5.86	102.60
SD26-11	27.50620	3.19	15.445	8.489	60.39	293.33	33.73	24.90	5.78	101.69
SD26-12	27.51580	4.17	15.673	8.467	62.95	345.58	33.78	24.89	5.60	99.01
SD26-13	27.52540	5.79	15.865	8.455	59.84	374.29	33.82	24.87	5.51	97.89
SD26-14	27.53620	7.47	16.039	8.448	58.51	401.94	33.85	24.86	5.46	97.40
SD26-15	27.54530	8.44	16.260	8.440	56.89	431.56	33.90	24.84	5.38	96.31
SD26-16	27.55340	9.33	16.276	8.442	57.34	425.75	33.89	24.84	5.42	97.10
SD26-17	27.56000	10.71	16.391	8.440	54.35	433.54	33.92	24.83	5.41	97.09
SD26-18	27.58040	12.60	16.496	8.445	60.39	465.46	33.92	24.80	5.50	98.95
SD26-19	27.60540	14.99	16.723	8.440	50.17	459.98	34.00	24.81	5.43	98.20
SD26-20	27.61900	17.83	17.020	8.443	43.64	473.41	34.06	24.79	5.39	98.12
SD26-21	27.63750	20.49	17.092	8.445	45.33	478.26	34.08	24.79	5.40	98.41
SD26-22	27.65360	22.79	17.430	8.452	43.67	491.31	34.16	24.77	5.37	98.54
SD26-23	27.66800	25.19	17.890	8.460	39.83	507.39	34.25	24.73	5.30	98.14
SD26-24	27.68060	27.63	18.132	8.463	37.33	513.56	34.30	24.70	5.29	98.50
SD26-25	27.69200	30.06	18.549	8.467	23.67	527.53	34.31	24.61	4.80	90.02
SD26-26	27.70890	33.57	18.431	8.446	28.34	533.02	34.19	24.55	4.38	81.89
SD26-27	27.72080	37.64	19.469	8.491	20.05	557.73	34.51	24.53	4.21	80.52

Parameter	Flow Thru UVF	Flow Thru Chl-a	Flow Thru Cu Jalpaite ISE	Flow Thru Cu Chalcog. ISE	Flow Thru pH	pH2 TMA Cu	pH2 TMA Zn	total Cu	diss. Cu	total Zn	diss. Zn	TSS
Data Units	(volts)	(ug/L)	(pCu)	(pCu)	(NBS)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(mg/L)
Data Type	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Lab	Lab	Lab	Lab	Lab
Data Source	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments												
Sample ID												
SD26-01	0.000	0.026	12.96	11.77	8.178	NS	0.4	0.1	0.1	0.10	0.26	0.66
SD26-02	0.003	0.030	12.88	11.70	8.173	1.0	0.6	0.2	0.1	0.31	0.29	1.26
SD26-03	0.003	0.028	12.86	11.69	8.161	-0.1	1.4	0.3	0.2	0.77	0.63	1.24
SD26-04	0.006	0.030	13.50	12.04	8.140	0.0	1.5	0.6	0.4	1.6	1.31	2.25
SD26-05	0.014	0.029	13.34	11.95	8.140	-0.1	NS	0.4	0.3	1.0	0.66	7.57
SD26-06	0.667	0.036	11.86	11.09	8.100	3.9	10.9	4.5	3.4	14.3	13.9	1.69
SD26-07	0.003	0.030	12.70	11.58	8.111	-0.2	NS	0.4	0.2	1.2	0.84	2.23
SD26-08	0.131	0.030	12.73	11.61	8.092	1.5	3.7	0.9	0.6	3.3	2.6	3.07
SD26-09	0.974	0.037	12.28	11.36	8.047	3.5	11.5	3.7	2.7	12.0	12.8	2.80
SD26-10	0.449	0.031	12.58	11.50	8.071	1.4	5.5	1.6	1.1	6.6	5.7	2.13
SD26-11	0.602	0.032	12.60	11.53	8.064	1.4	7.83	1.9	1.2	7.5	6.7	2.83
SD26-12	0.863	0.030	12.56	11.52	8.045	1.7	7.14	2.3	1.7	9.2	9.3	3.58
SD26-13	1.023	0.030	12.52	11.49	8.038	1.9	NS	2.8	2.0	10.9	11.0	4.06
SD26-14	1.171	0.031	12.50	11.49	8.036	2.3	8.2	2.7	2.1	11.4	11.9	2.78
SD26-15	1.353	0.031	12.49	11.48	8.032	2.1	5.6	3.3	2.4	12.8	12.7	2.98
SD26-16	1.314	0.032	12.50	11.48	8.038	2.3	NS	3.1	2.3	12.7	12.5	5.12
SD26-17	1.371	0.033	12.49	11.48	8.042	2.1	NS	3.2	2.4	12.5	12.8	2.33
SD26-18	1.509	0.037	12.49	11.49	8.055	3.5	10.6	3.2	2.7	12.8	12.7	2.25
SD26-19	1.525	0.040	12.57	11.54	8.055	3.4	9.1	3.3	2.8	12.3	12.5	2.51
SD26-20	1.638	0.044	12.60	11.56	8.061	2.6	10.3	3.5	2.9	12.1	11.6	3.85
SD26-21	1.651	0.044	12.58	11.55	8.064	2.4	8.7	3.4	2.9	11.7	11.4	3.71
SD26-22	1.744	0.048	12.64	11.59	8.073	2.4	7.8	3.3	2.8	10.5	10.0	3.29
SD26-23	1.891	0.053	12.71	11.65	8.083	2.08	7.1	3.0	2.3	9.6	8.4	6.57
SD26-24	1.986	0.054	12.75	11.69	8.088	2.3	6.3	3.1	2.2	8.6	7.5	4.64
SD26-25	2.220	0.063	12.89	11.81	8.096	1.3	6.0	2.8	1.8	6.8	4.6	7.93
SD26-26	2.154	0.058	12.81	11.74	8.085	2.2	7.2	3.1	2.2	8.0	6.6	4.12
SD26-27	2.592	0.074	12.90	11.81	8.133	1.6	3.9	2.6	1.7	5.9	3.3	9.05

Parameter	Bacterial Production	DOC	Total Alkalinity	Chloro-phyll	Phaeo-pigments	Bact. Abund.	Cyano Abund.	NO_3	PO_4	Si	NO_2	NH_3
Data Units	(ugC/L/d)	(mg/L)	um kg^{-1}	(mg m^{-3})	(mg m^{-3})	(ml^{-1})	(ml^{-1})	(uM)	(uM)	(uM)	(uM)	(uM)
Data Type	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
Data Source	NRL Boyd	NRL Boyd	UABC Ayon	SIO Holm-Hansen	SIO Holm-Hansen	SIO Holm-Hansen	SIO Holm-Hansen	SIO ODF	SIO ODF	SIO ODF	SIO ODF	SIO ODF
Comments												
Sample ID												
SD26-01	4.47	0.88	NS	0.73	0.34	NS	NS	0.11	0.08	0.2	0	0.13
SD26-02	6.86	1.00	2219	0.92	0.47	NS	NS	0.11	0.13	0.3	0	0.18
SD26-03	9.28	0.76	2208	0.98	0.61	NS	NS	0.18	0.3	0.7	0.01	0.3
SD26-04	13.55	1.14	NS	1.04	0.69	NS	NS	0.31	0.4	1.7	0.04	0.67
SD26-05	14.19	0.85	NS	0.98	0.76	NS	NS	0.32	0.43	2.1	0.04	0.48
SD26-06	12.20	1.05	2237	1.20	0.84	NS	NS	0.2	0.48	3.6	0.04	0.51
SD26-07	10.18	0.86	NS	1.23	0.67	NS	NS	0.16	0.36	1.4	0.03	0.34
SD26-08	12.54	0.88	2206	1.14	0.61	NS	NS	0.21	0.49	2.6	0.04	0.51
SD26-09	11.69	1.16	2233	1.56	0.81	NS	NS	0.36	0.64	4	0.08	0.83
SD26-10	8.18	1.12	2253	1.15	0.63	NS	NS	0.66	1.04	2.1	0.03	0.56
SD26-11	8.75	1.08	2219	1.33	0.61	NS	NS	0.16	0.45	1.8	0.03	0.56
SD26-12	9.56	1.26	2201	1.17	0.57	NS	NS	0.32	0.62	3.2	0.04	0.75
SD26-13	9.02	1.27	2229	1.11	0.62	NS	NS	0.37	0.75	3.8	0.06	0.93
SD26-14	7.73	1.14	2213	1.05	0.61	NS	NS	0.25	0.55	2.9	0.04	0.74
SD26-15	10.74	1.30	2247	0.96	0.61	NS	NS	0.67	0.96	2.7	0.04	0.91
SD26-16	11.60	1.44	2222	1.12	0.71	NS	NS	0.33	0.71	4.4	0.05	0.76
SD26-17	5.39	1.28	2295	0.90	0.61	NS	NS	0.29	0.65	3.6	0.08	0.86
SD26-18	7.19	1.36	2256	1.42	0.55	NS	NS	0.34	0.75	4.2	0.16	0.79
SD26-19	10.09	1.44	2272	1.31	0.82	NS	NS	0.22	0.86	4.1	0.05	0.64
SD26-20	12.26	1.42	2249.40	1.56	1.02	NS	NS	0.07	0.77	3.8	0.04	0.46
SD26-21	16.78	1.58	2318	1.69	1.05	NS	NS	0.12	0.77	4.3	0.04	0.4
SD26-22	20.91	1.48	2277	1.75	1.16	NS	NS	0.05	0.76	4.3	0.09	0.4
SD26-23	16.99	1.57	2259	1.95	1.38	NS	NS	0.06	0.79	5	0.06	0.47
SD26-24	27.25	1.59	2359	2.25	1.41	NS	NS	0.1	0.74	5.9	0.05	0.5
SD26-25	32.03	1.81	2363	2.49	1.79	NS	NS	0.01	0.86	7.3	0.04	0.52
SD26-26	26.74	1.58	2322	2.65	1.56	NS	NS	0.17	0.8	6.8	0.07	0.77
SD26-27	30.11	1.79	2394	3.05	2.07	NS	NS	0.03	0.9	9.7	0.06	0.54

Parameter	Complex. Capacity	D. excen-tricus EC50	M. gallopro-vincialis EC50	S. purpur-atus EC50	L_{tot}	K_L
Data Units	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	
Data Type	Lab	Lab	Lab	Lab	Lab	Lab
Data Source	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments	by ISE	Toxicity	Toxicity	Toxicity	by DPASV	by DPASV
Sample ID						
SD26-01	17.29	NS	7.06	13.16	7.21	7.80E+07
SD26-02	8.16	NS	11.95	16.22	5.90	9.35E+07
SD26-03	11.77	NS	9.86	17.11	9.84	2.83E+07
SD26-04	9.16	NS	9.85	20.25	7.37	1.06E+08
SD26-05	9.12	NS	12.54	16.51	8.24	7.83E+07
SD26-06	NS	NS	NS	NS	NS	NS
SD26-07	NS	NS	NS	NS	NS	NS
SD26-08	NS	NS	NS	NS	NS	NS
SD26-09	NS	NS	13.12	24.71	NS	NS
SD26-10	NS	NS	NS	NS	NS	NS
SD26-11	10.48	NS	15.13	NS	8.65	7.20E+07
SD26-12	9.74	NS	12.27	23.00	9.39	3.13E+07
SD26-13	NS	NS	NS	NS	NS	NS
SD26-14	14.33	NS	NS	NS	6.73	6.50E+07
SD26-15	13.95	NS	11.29	23.00	10.26	5.44E+07
SD26-16	NS	NS	NS	NS	NS	NS
SD26-17	11.31	NS	NS	NS	9.88	2.68E+07
SD26-18	13.10	NS	16.81	29.45	NS	NS
SD26-19	NS	NS	NS	NS	NS	NS
SD26-20	11.09	NS	NS	NS	9.08	5.09E+07
SD26-21	14.84	NS	19.23	26.88	10.00	2.51E+07
SD26-22	NS	NS	NS	NS	NS	NS
SD26-23	16.13	NS	16.88	30.03	11.29	7.81E+07
SD26-24	NS	NS	NS	NS	NS	NS
SD26-25	14.06	NS	18.01	35.33	8.66	5.85E+07
SD26-26	15.46	NS	15.53	27.57	10.87	5.86E+07
SD26-27	17.62	NS	24.32	44.46	8.59	7.30E+07

SD35: May 2002

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Parameter	Time	Residence Time	In Situ Temp	In Situ pH	In Situ Light Trans. @ 670 nm	In Situ UVF	In Situ Salinity	Density	In Situ Oxygen	In Situ Oxygen
Data Units	Day of May 2002	(days)	(^{o}C)	(NBS)	(%)	(ug/L DFM)	(psu)	(sigma-t)	(mg/L)	(% sat.)
Data Type		model	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ	In Situ
Data Source	SPAWAR	SD1D	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments										
Sample ID										
SD26-01	14.37030	0.00	14.576	8.181	68.45	214.17	33.65	25.02	NS	NS
SD26-02	14.38320	0.05	14.210	8.132	64.04	218.01	33.66	25.10	NS	NS
SD26-03	14.39430	0.15	14.655	8.133	58.97	214.38	33.67	25.02	NS	NS
SD26-04	14.40530	0.36	14.712	8.130	64.14	211.81	33.68	25.01	NS	NS
SD26-05	14.41960	0.74	15.096	8.139	62.72	228.50	33.69	24.94	NS	NS
SD26-06	14.43890	NS	18.032	8.128	61.07	343.23	33.84	24.38	NS	NS
SD26-07	14.47440	1.18	15.468	8.118	61.53	249.19	33.72	24.88	NS	NS
SD26-08	14.48350	1.63	16.024	8.122	55.23	275.58	33.75	24.78	NS	NS
SD26-09	14.49540	NS	18.249	8.113	51.14	386.27	33.90	24.37	NS	NS
SD26-10	14.50700	2.30	17.001	8.115	53.32	314.34	33.81	24.60	NS	NS
SD26-11	14.51580	3.19	17.561	8.112	48.19	335.51	33.86	24.51	NS	NS
SD26-12	14.52430	4.17	18.128	8.103	49.16	367.07	33.92	24.41	NS	NS
SD26-13	14.53390	5.79	18.932	8.090	45.56	390.92	34.00	24.27	NS	NS
SD26-14	14.54380	7.47	19.115	8.078	48.28	407.59	34.04	24.26	NS	NS
SD26-15	14.55210	8.44	19.298	8.081	47.87	405.41	34.04	24.21	NS	NS
SD26-16	14.55870	9.33	19.186	8.071	51.69	400.33	34.03	24.23	NS	NS
SD26-17	14.56550	10.71	19.451	8.069	49.96	412.54	34.06	24.19	NS	NS
SD26-18	14.58130	12.60	20.029	8.061	51.30	430.38	34.12	24.09	NS	NS
SD26-19	14.60100	14.99	20.421	8.054	46.62	424.93	34.20	24.04	NS	NS
SD26-20	14.62400	17.83	21.116	8.042	50.19	446.85	34.35	23.96	NS	NS
SD26-21	14.64970	20.49	21.398	8.043	45.52	464.10	34.44	23.96	NS	NS
SD26-22	14.66590	22.79	21.753	8.045	46.66	485.24	34.59	23.97	NS	NS
SD26-23	14.68040	25.19	22.187	8.050	46.71	491.68	34.72	23.95	NS	NS
SD26-24	14.69380	27.63	22.526	8.066	49.82	496.58	34.80	23.92	NS	NS
SD26-25	14.70570	30.06	22.976	8.086	49.34	510.02	34.96	23.91	NS	NS
SD26-26	14.71860	33.57	22.940	8.076	47.42	516.24	34.97	23.93	NS	NS
SD26-27	14.71350	37.64	23.565	8.101	45.89	541.78	35.23	23.94	NS	NS

Parameter	Flow Thru UVF	Flow Thru Chl-a	Flow Thru Cu Jalpaite ISE	Flow Thru Cu Chalcog. ISE	Flow Thru pH	pH2 TMA Cu	pH2 TMA Zn	total Cu	diss. Cu	total Zn	diss. Zn	TSS
Data Units	(volts)	(ug/L)	(pCu)	(pCu)	(NBS)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(mg/L)
Data Type	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Flow Thru	Lab	Lab	Lab	Lab	Lab
Data Source	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments												
Sample ID												
SD26-01	0.136	1.310	12.46	12.82	7.946	0.2	1.1	0.4	0.3	0.84	0.46	1.86
SD26-02	0.148	1.015	12.47	12.72	7.902	0.2	1.5	0.4	0.3	1.04	0.45	2.22
SD26-03	0.107	0.836	12.50	12.78	7.901	0.2	1.1	0.5	0.3	1.23	0.45	2.68
SD26-04	0.110	0.864	12.65	12.92	7.886	0.2	1.5	0.6	0.4	1.5	0.66	2.21
SD26-05	0.186	0.846	12.60	12.75	7.893	0.3	1.8	0.9	0.6	2.6	1.19	2.34
SD26-06	0.792	0.714	12.07	11.73	7.888	2.4	9.2	4.2	3.1	7.8	8.4	2.48
SD26-07	0.305	0.915	12.35	12.56	7.885	0.9	2.3	1.0	0.7	2.4	1.41	2.44
SD26-08	0.434	0.978	12.43	12.59	7.887	0.7	NS	1.2	0.8	2.4	1.7	3.03
SD26-09	0.982	0.821	12.27	12.24	7.876	2.2	5.4	3.0	2.4	5.6	6.0	3.46
SD26-10	0.635	0.992	12.40	12.58	7.883	1.0	3.7	1.8	1.3	5.3	2.7	3.23
SD26-11	0.749	0.935	12.45	12.61	7.876	0.8	5.14	2.0	1.4	5.4	3.0	3.78
SD26-12	0.911	0.972	12.48	12.61	7.871	0.7	4.29	2.4	1.7	6.6	3.7	3.67
SD26-13	1.067	0.904	12.47	12.60	7.862	0.7	5.46	2.6	1.9	7.7	6.3	4.09
SD26-14	1.157	0.904	12.46	12.55	7.856	0.5	5.6	2.7	2.0	8.3	4.7	3.77
SD26-15	1.155	0.917	12.45	12.53	7.860	0.4	NS	2.7	2.1	7.9	4.3	3.82
SD26-16	1.104	0.859	12.45	12.52	7.853	NS	6.0	2.6	2.0	7.5	3.8	3.40
SD26-17	1.189	0.849	12.44	12.50	7.851	NS	5.8	2.7	2.1	6.6	4.4	3.58
SD26-18	1.297	0.782	12.45	12.50	7.851	0.5	6.4	2.9	2.2	8.8	8.1	3.44
SD26-19	1.264	0.835	12.47	12.58	7.850	0.6	5.7	2.8	2.2	6.2	7.2	3.96
SD26-20	1.390	0.784	12.47	12.52	7.844	2.4	6.7	3.1	2.5	7.3	7.5	3.56
SD26-21	1.498	0.856	12.45	12.51	7.846	1.8	6.0	3.4	2.6	8.9	8.0	4.10
SD26-22	1.637	0.882	12.48	12.52	7.851	1.6	5.6	3.5	2.7	7.1	7.9	3.96
SD26-23	1.700	0.858	12.51	12.58	7.856	1.35	5.5	3.6	2.8	7.3	4.5	3.95
SD26-24	1.736	0.838	12.57	12.64	7.873	1.2	5.1	3.8	2.7	6.1	4.1	3.60
SD26-25	1.854	0.880	12.62	12.69	7.896	1.0	4.7	3.9	2.5	6.5	3.6	3.65
SD26-26	1.895	0.972	12.65	12.69	7.890	0.9	NS	4.0	2.5	5.9	2.9	3.87
SD26-27	2.145	1.030	12.66	12.74	7.908	1.0	4.2	2.7	2.4	5.3	2.5	4.05

Parameter	Bacterial Production	DOC	Total Alkalinity	Chloro-phyll	Phaeo-pigments	Bact. Abund.	Cyano Abund.	NO_3	PO_4	Si	NO_2	NH_3
Data Units	(ugC/L/d)	(mg/L)	um kg^{-1}	(mg m^{-3})	(mg m^{-3})	(ml^{-1})	(ml^{-1})	(uM)	(uM)	(uM)	(uM)	(uM)
Data Type	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab	Lab
Data Source	NRL Boyd	NRL Boyd	UABC Ayon	SIO Holm-Hansen	SIO Holm-Hansen	SIO Holm-Hansen	SIO Holm-Hansen	SIO ODF	SIO ODF	SIO ODF	SIO ODF	SIO ODF
Comments												
Sample ID												
SD26-01	5.32	2.01	2227	4.41	0.96	1526993	62941	0.96	0.58	7.8	0.06	0.33
SD26-02	5.86	1.55	2224	3.26	1.12	1684618	54184	1.25	0.63	6.8	0.07	0.32
SD26-03	5.44	1.94	2228	2.35	1.24	1852094	47041	1.45	0.62	6.9	0.08	0.35
SD26-04	7.02	1.68	2218.70	2.12	1.09	1704321	41869	1.36	0.59	7.4	0.07	0.39
SD26-05	5.37	2.02	2230	2.32	1.09	NS	NS	1.61	0.69	8.5	0.08	0.51
SD26-06	5.27	1.66	2244	1.47	0.69	2384079	13300	0.1	0.57	10.3	0.03	0.4
SD26-07	5.00	1.55	2203	2.41	0.97	2147641.28	51474.43	1.07	0.63	8.1	0.07	0.42
SD26-08	4.38	1.91	2228	2.97	1.23	2837251	43593	0.62	0.63	8.5	0.06	0.56
SD26-09	9.02	1.73	2255	1.75	0.91	2994876	48026	0.01	0.59	10.6	0.02	0.23
SD26-10	5.61	1.81	2240	2.65	1.04	2492446	35958	0.25	0.64	9.3	0.04	0.56
SD26-11	5.87	1.82	2263	2.67	1.05	2579319	26107	0.12	0.62	9.7	0.03	0.4
SD26-12	7.28	2.78	2262	2.47	0.96	2531852	13792	0.08	0.63	10.6	0.03	0.44
SD26-13	6.62	1.90	2270	1.91	0.96	2443188.25	6649.81	0.05	0.64	10.9	0.02	0.23
SD26-14	4.30	2.06	2273	2.16	1.03	2462891	4679	0	0.67	11.1	0.02	0.2
SD26-15	5.64	3.58	2262	2.20	1.00	2451945	4187	0	0.67	11.2	0.02	0.18
SD26-16	6.83	2.28	2258	1.91	0.96	3172204	5911	0.01	0.64	10.6	0.02	0.24
SD26-17	1.55	2.00	NS	1.72	0.83	2719032	3448	0.11	0.68	11.2	0.03	0.27
SD26-18	4.15	2.08	2280	1.41	0.84	2669774	3448	0	0.72	11.9	0.02	0.23
SD26-19	4.70	2.06	2290	1.49	0.82	3625376.11	1231.45	0	0.75	11.5	0.02	0.21
SD26-20	6.79	2.29	2268.90	1.40	0.86	3063837	0	0	0.8	11.9	0.02	0.19
SD26-21	5.02	2.38	2288	1.45	0.96	3073688.44	0.00	0	0.83	12.2	0.02	0.19
SD26-22	3.84	2.45	2333	1.51	0.99	3556415	0	0	0.9	13	0.02	0.22
SD26-23	1.78	3.53	2321	1.60	1.04	3842111	0	0	0.93	13.8	0.02	0.2
SD26-24	6.19	3.72	2314	1.35	1.02	4275579	0	0	0.92	13.9	0.02	0.19
SD26-25	7.85	2.49	2329	1.46	1.01	4039141.86	0.00	0	0.95	14.7	0.02	0.17
SD26-26	8.50	2.64	2340	1.90	1.38	4137658	0	0	0.94	15.4	0.02	0.19
SD26-27	7.07	3.15	2342	1.49	1.32	3428345	0	0	0.98	15.4	0.03	0.37

Parameter	Complex. Capacity	D. excen-tricus EC50	M. gallopro-vincialis EC50	S. purpur-atus EC50	L_{tot}	K_L
Data Units	(ug/L)	(ug/L)	(ug/L)	(ug/L)	(ug/L)	
Data Type	Lab	Lab	Lab	Lab	Lab	Lab
Data Source	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR	SPAWAR
Comments	by ISE	Toxicity	Toxicity	Toxicity	by DPASV	by DPASV
Sample ID						
SD26-01	18.28	NS	10.84	NS	9.21	4.05E+07
SD26-02	14.36	NS	12.63	NS	7.79	4.42E+07
SD26-03	11.14	NS	9.15	NS	11.74	3.58E+07
SD26-04	13.57	NS	2.95	NS	8.12	6.15E+07
SD26-05	NS	NS	NS	NS	NS	NS
SD26-06	NS	NS	NS	NS	NS	NS
SD26-07	NS	NS	NS	NS	NS	NS
SD26-08	NS	NS	NS	NS	NS	NS
SD26-09	NS	NS	6.15	NS	NS	NS
SD26-10	NS	NS	NS	NS	NS	NS
SD26-11	NS	NS	NS	NS	NS	NS
SD26-12	16.30	NS	10.47	NS	8.86	1.02E+08
SD26-13	NS	NS	NS	NS	NS	NS
SD26-14	NS	NS	NS	NS	NS	NS
SD26-15	11.84	NS	7.92	NS	10.75	2.75E+07
SD26-16	NS	NS	NS	NS	NS	NS
SD26-17	NS	NS	NS	NS	NS	NS
SD26-18	16.24	NS	14.08	NS	6.71	1.05E+08
SD26-19	NS	NS	NS	NS	NS	NS
SD26-20	NS	NS	NS	NS	NS	NS
SD26-21	10.83	NS	12.92	NS	8.93	4.22E+07
SD26-22	NS	NS	NS	NS	NS	NS
SD26-23	13.66	NS	6.58	NS	13.04	2.78E+07
SD26-24	NS	NS	NS	NS	NS	NS
SD26-25	12.81	NS	12.58	NS	5.93	4.21E+07
SD26-26	12.05	NS	13.45	NS	12.72	4.55E+07
SD26-27	13.92	NS	15.82	NS	NS	NS

APPENDIX B: LIST OF TECHNICAL PUBLICATIONS

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The manuscripts listed below have all progressed toward publication as result of the research developed in this effort. These manuscripts are either published or are in press at this time:

Blake, A.C., D.B. Chadwick, A. Zirino and I. Rivera-Duarte, 2004. Spatial and temporal variations in copper speciation in San Diego Bay. Estuaries 27(3): 437-447.

Boyd T.J., D.M. Wolgast, I. Rivera-Duarte, O. Holm-Hansen, C.D. Hewes, A. Zirino, and D.B. Chadwick, 2005. Effects of dissolved and complexed copper on heterotrophic bacterial production in San Diego Bay. Microbial Ecology (in press).

Chadwick, D.B., Zirino, A., Rivera-Duarte, I., Katz, C.N., and Blake, A.C., 2004. Modeling the mass balance and fate of copper in San Diego Bay. Limnology & Oceanography, 49: 355-366.

Rivera-Duarte, I.; Zirino, A., 2004. Response of the Cu(II) ion selective electrode to Cu titration in artificial and natural shore seawater and in the measurement of the Cu complexation capacity. Environmental Science & Technology, 38(11): 3139-3147.

Rivera-Duarte, I., G. Rosen, D. Lapota, D.B. Chadwick, L. Kear-Padilla, and A. Zirino, 2005. Copper toxicity to larval stages of three marine invertebrates and copper complexation capacity in San Diego Bay, California. Environmental Science & Technology 39(6): 1542-1546.

Rosen, G., I. Rivera-Duarte, L. Kear-Padilla, and D.B. Chadwick, 2005. Use of laboratory toxicity tests with bivalve and echinoderm embryos to evaluate the bioavailability of copper to in San Diego Bay, California, USA. Environmental Toxicology and Chemistry 24(2): 415-422.

The following papers are in draft form and will be submitted in the near future:

Holm-Hansen, O., 2005. Phytoplankton and Bacterial concentrations and characteristics in San Diego Bay (California) in relation to concentrations of dissolved and total Copper and Zinc (in prep).

Gieskes, J., C. Mahn, P. Kolinko, and J. Ho., 2005. The geochemistry of trace metals in San Diego Bay sediments (in prep).

Wang, P.F., B. Chadwick, I. Rivera-Duarte, and A. Zirino, 2005. Application of the two-dimensional Tidal Residual Intertidal Mudflat (TRIM2D) model to the transport, speciation and fate of copper in San Diego Bay (in prep).

The following papers are in early development and will be submitted in the near future (Note – drafts of these papers are not included in the Appendix pending further development).

Chadwick, B., I. Rivera-Duarte, G. Rosen, T. Boyd, A. Zirino, L. Kear. 2005. Modeling copper speciation and toxicity in San Diego Bay (in prep).

Rivera-Duarte, I., D.B. Chadwick, A. Zirino, and S. Sañudo-Wilhelmy. 2005 Distributions of Ag, Cd, Co, Cu, Ni, Pb, V and Zn in San Diego Bay (in prep).

The following are Published Technical Abstracts:

Chadwick D.B., Rivera-Duarte I., Blake A., Wang P.F., Rosen G., Zirino A., Boyd T., Gieskes J., and Holm-Hansen, O.. Modeling copper speciation, fate and effects in DoD harbors. "Partners in Environmental Technology" Technical Symposium and Workshop, Strategic Environmental Research and Development Program and Environmental Security Technology Certification Program, Washington, DC, November 30 to December 2, 2004.

Chadwick D.B., Rivera-Duarte I., Rosen G., Katz C., Blake A., Wang P.F., Boyd T., and Zirino A. Management of copper loadings in heavily used bays. "Partners in Environmental Technology" Technical Symposium and Workshop, Strategic Environmental Research and Development Program and Environmental Security Technology Certification Program, Washington, DC, December 2-4, 2003.

Rivera-Duarte I., Rosen G., Chadwick D.B., Kear-Padilla L., and Zirino A. Speciation and bioavailability of copper in San Diego Bay. Free copper ion as the main factor to study the effect of copper leaching from antifouling paints. Prevention of Pollution from Ships, Shipyards, Drydocks, Ports and Harbors International Symposium, New Orleans, LA, November 5-7, 2003.

Rosen G., Rivera-Duarte I., Kear-Padilla L., and Chadwick D.B. Effects of copper on marine invertebrate larvae in surface water from San Diego Bay, CA. Prevention of Pollution from Ships, Shipyards, Drydocks, Ports and Harbors International Symposium, New Orleans, LA, November 5-7, 2003.

Chadwick D.B., Wang P.-F., Rivera-Duarte I., and Zirino A. Harbor modeling of fate and speciation of copper: San Diego Bay case study. Prevention of Pollution from Ships, Shipyards, Drydocks, Ports and Harbors International Symposium, New Orleans, LA, November 5-7, 2003.

Rivera-Duarte I., Chadwick D.B., Rosen G., Kear-Padilla L., and Zirino A. Chemical speciation controlling toxicity of copper or zinc in coastal embayments. Society of Environmental Toxicology and Chemistry, Asia Pacific Conference, Christchurch, New Zealand, September 28 to October 1, 2003.

Chadwick D.B., Rivera-Duarte I., Zirino A. Blake A., and Katz C. Modeling as an Environmental Management Tool for Copper Release to San Diego Bay, California. Society of Environmental Toxicology and Chemistry, Asia Pacific Conference, Christchurch, New Zealand, September 28 to October 1, 2003.

Chadwick D.B., Rivera-Duarte I., Rosen G., Wang P.F., and Zirino A. Evaluation and modeling of environmental and toxicological conditions of copper and zinc in coastal basins. "Partners in Environmental Technology" Technical Symposium and Workshop, Strategic

Environmental Research and Development Program and Environmental Security Technology Certification Program, Washington, DC, December 3-5, 2002.

Chadwick D.B., Rivera-Duarte I., and Zirino A. Mass Balance and Speciation of Copper in San Diego Bay, California. Society of Environmental Toxicology and Chemistry 23rd Annual Meeting, Salt Lake City, Utah, November 16-20, 2002.

Chadwick D.B., Rivera-Duarte I., and Zirino A. Modeling of copper toxicity from chemical speciation and physicochemical conditions in San Diego Bay. California and the World Ocean '02 Conference, "California's Ocean Resources: An Agenda for the Future," Santa Barbara, California, October 27-30, 2002.

Rivera-Duarte I., Rosen G., Chadwick D.B., Lapota D., and Zirino A. Effects of Copper in Heavily Impacted Coastal Embayments: Chemical Speciation and Toxicity in San Diego Bay. 11th International Congress on Marine Corrosion and Biofouling, University of San Diego, San Diego, California, July 22-26, 2002.

Chadwick D.B., Rivera-Duarte I., Zirino A., Wang P.F., Katz C., and Carlson A. Modeling the Mass Balance and Fate of Copper in San Diego Bay. 11th International Congress on Marine Corrosion and Biofouling, University of San Diego, San Diego, California, July 22-26, 2002.

Chadwick D.B., Rivera-Duarte I., Rosen G., and Zirino A. A whole-basin approach for the study of toxicity of copper in coastal embayments. "Partners in Environmental Technology" Technical Symposium and Workshop, Strategic Environmental Research and Development Program and Environmental Security Technology Certification Program, Washington, DC, November 27-29, 2001.

Rivera-Duarte I., Rosen G, Chadwick DB, Lapota D, and Zirino A. The relationship between complexation capacity and toxicity of copper to marine invertebrates. 16th Biennial Conference "An Estuarine Odyssey" of the Estuarine Research Federation, St. Pete Beach, Florida, November 7-8, 2001.

Rivera-Duarte I., G. Rosen, D. Lapota and A. Zirino. Free copper ion activity, complexation capacity and toxicity in San Diego Bay waters. Office of Naval Research Second Copper Workshop, Annapolis, Maryland, November 1-2, 2000.